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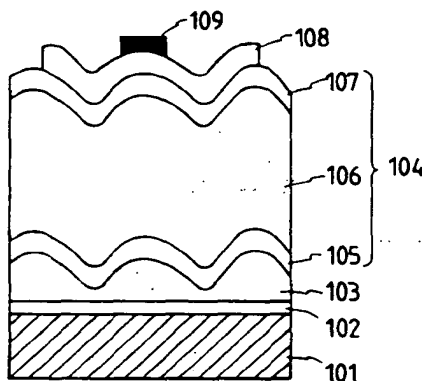
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54 Photovoltaic device and method for producing the same.

57 A photovoltaic device comprises a metal with a smooth surface; a transparent layer formed on the smooth surface; and a photoelectric conversion layer formed on the transparent layer. The transparent layer has an irregular surface at a side opposite to the smooth surface.

FIG. 1



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BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a photovoltaic device of a high conversion efficiency, high reliability and satisfactory mass producibility, and a method for producing the same, and it also relates to a secondary battery, an artificial satellite, a roofing material, a solar cell module, an automobile or the like, utilizing a solar cell as an example of said photovoltaic device.

Related Background Art

For the future energy source of the human beings, there are involved various problems in the total reliance on the fossil fuels such as petroleum and coal of which use is considered to result in warming of the earth because of the generated carbon dioxide etc., and on the nuclear power which cannot be freed from the danger of radioactivity in case of an unpredictable accident or even in the ordinary operation. In contrast, the solar cell utilizing the solar light as the energy source has very little influence on the environment of the earth, and is expected for wider applications. At present, however, there are some drawbacks that hinder practical use of such solar cells.

For solar power generation there has mostly been utilized monocrystalline or polycrystalline silicon. However, such solar cell as an example of the photovoltaic cells, requires a large amount of energy and time for crystal growth and also requires complex subsequent steps, so that the mass production is difficult to achieve and the supply at a low price has therefore been difficult. On the other hand, there have been conducted active research and development on so-called thin film semiconductor photovoltaic devices utilizing amorphous silicon (hereinafter represented as a-Si), or compound semiconductors such as CdS or CuInSe₂. Such photovoltaic devices can be obtained by forming necessary semiconductor layers on an inexpensive substrate such as glass or stainless steel with a relatively simple process, and have therefore possibility of cost reduction. However, such thin film semiconductor photovoltaic devices have not been employed in practice because their conversion efficiency on light is lower than that of the crystalline silicon photovoltaic devices, and also their reliability for prolonged use has been low. For this reason, there have been made various attempts for improving the performance of the thin film semiconductor photovoltaic devices.

An attempt consists of a rear reflective layer for returning the light, not absorbed by the semiconductor layer, again to said semiconductor layer, in order to achieve effective utilization of the incident light. For this purpose, in case the light is introduced through a transparent substrate, the electrode formed on the surface of the semiconductor layer is composed of a highly reflective metal such as silver (Ag), aluminum (Al) or copper (Cu). Also in case the light is introduced from the top side of the semiconductor layer, a similar metal layer for increasing the reflectance is formed on the substrate, before the formation of said semiconductor layer. Also a transparent layer with a suitable optical property may be provided between the metal layer and the semiconductor layer, for further improving the reflectance by multiple interference. Fig. 4A shows the reflectances in case such transparent layer is not present between silicon and various metals, and Fig. 4B shows the simulated results of improvement in reflectance, in case a zinc oxide (ZnO) layer is provided as such transparent layer between silicon and various metals.

Such transparent layer is also effective in improving the reliability of the photovoltaic device. The Japanese Patent Publication No. 60-41678 describes that such transparent layer prevents alloy formation between the semiconductor and the metal layer. Also the U.S. Patents Nos. 4,532,372 and 4,598,306 describe that a transparent layer with a suitable electrical resistance prevents the generation of excessive current between the electrodes even in case of a shortcircuiting in the semiconductor layer.

Another attempt for improving the conversion efficiency of the photovoltaic device consists of employing a texture, having fine irregularities, on the surface of the photovoltaic device and/or the interface with the rear reflective layer. In such configuration, the light is scattered on the surface of the photovoltaic device and/or at the interface with the rear reflective layer and is confined in the semiconductor (phototrapping effect), whereby it is effectively absorbed therein. In case the substrate is transparent, the texture is formed on the surface of a transparent electrode, for example of tin oxide (SnO₂) formed on the substrate. Also in case the light is introduced from the top side of the semiconductor, the texture is formed on the surface of the metal layer employed as the rear reflective layer. M. Harasaka, K. Suzuki, K. Nakatani, M. Asano, M. Yano and H. Okaniwa reported that an irregular texture for rear reflecting layer could be obtained by Al deposition under control of the substrate temperature and the deposition rate (Solar Cell Materials 20(1990), pp. 99 - 110). Fig. 5 shows an example of increase of absorption of the incident light, through the use of a

rear reflective layer with such texture, wherein a curve (a) indicates the spectral sensitivity of an a-Si photovoltaic device employing smooth Ag as the metal layer, while a curve (b) indicates the spectral sensitivity of a similar device employing Ag of irregular texture.

It is also possible to combine the concept of the rear reflective layer consisting of a metal layer and a transparent layer, and the concept of texture structure. The U.S. Patent No. 4,419,533 discloses the concept of the rear reflective layer in which the surface of the metal layer has a textured structure and a transparent layer is formed thereon. The light conversion efficiency of the solar cell, constituting an example of the photovoltaic device, is expected to be significantly improved by such combination. However, according to the experiences of the present inventors, such improvements have not been attained in most cases. Also under certain conditions of semiconductor deposition, the obtained solar cell does not enough reliability for the use under the conditions of high temperature and high humidity, despite the presence of the transparent layer. For these reasons, the thin film solar cells have not been employed in practical applications, though they have the possibility of low cost production.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a photovoltaic device comprising a metal with a smooth surface, a transparent layer formed on said smooth surface, and a photoelectric conversion layer formed on said transparent layer, wherein a surface of said transparent layer, opposite to said smooth surface, has irregular texture.

Another object of the present invention is to provide a photovoltaic device in which said transparent layer includes plural layer areas.

Still another object of the present invention is to provide a photovoltaic device wherein said transparent layer contains an impurity for increasing the electrical resistance.

Still another object of the present invention is to provide a photovoltaic device wherein said transparent layer is composed of ZnO, and said impurity is composed of Cu.

Still another object of the present invention is to provide a photovoltaic device wherein said transparent layer is composed of SnO₂, and said impurity is composed of Al.

Still another object of the present invention is to provide a photovoltaic device wherein, in said plural layer areas of the transparent layer, a layer area at the side of the metal has a higher specific resistivity than in a layer area at the side of the photoelectric conversion layer.

Still another object of the present invention is to provide a photovoltaic device in which said layer area at the side of the metal is thicker than said layer area at the side of the photoelectric conversion layer.

Still another object of the present invention is to provide a photovoltaic device in which a first layer area of the transparent layer, in contact with said smooth surface, has irregular texture on a surface thereof opposite to said smooth surface.

Still another object of the present invention is to provide a photovoltaic device in which said smooth surface has a pitch of irregular texture of 1000 Å or less, and the irregularly textured surface of said first layer area has a pitch of irregular texture within a range from 3000 to 20000 Å and irregularities of 500 Å.

Still another object of the present invention is to provide a photovoltaic device in which said transparent layer includes plural layer areas, wherein at least a layer area provided in contact with the smooth surface of said metal has a smooth surface at the side of said photoelectric conversion layer, and at least a layer area other than the above-mentioned layer area has irregular texture on a surface at the side of said photoelectric conversion layer.

Still another object of the present invention is to provide a photovoltaic device in which said smooth surface has a pitch of irregular texture of 1000 Å or less, said at least a layer area in contact with the metal has a pitch of irregular texture of 3000 Å or less on the smooth surface thereof at the side of said photoelectric conversion layer, and said layer area with irregular texture has a pitch of irregular texture within a range of 3000 to 20000 Å and irregularities within a range of 500 to 20000 Å.

Still another object of the present invention is to provide a photovoltaic device in which a surface of said photoelectric conversion layer, opposite to said transparent layer, has irregular texture comparable to that of said transparent layer.

Still another object of the present invention is to provide a method for producing a photovoltaic device including a metal with a smooth surface, a transparent layer and a photovoltaic layer, which comprises utilizing the difference in layer forming temperatures in case said transparent layer includes plural layer areas and a layer area in contact with the smooth surface of said metal has irregular surface texture, and, for said layer forming temperatures represented as T1 for a first layer, T2 for a second layer etc. from the side of said metal, satisfying a relation $T_1 > T_n$ between said first layer forming temperature T1 and at least

a forming temperature T_n for the second or subsequent layer.

Still another object of the present invention is to provide a method for producing a photovoltaic device including a metal with a smooth surface, a transparent layer and a photovoltaic layer, which comprises utilizing the difference in layer area forming temperatures in case said transparent layer includes plural layer areas and at least a layer area other than the layer area in contact with said smooth surface of the metal has irregular surface texture, and, for said layer area forming temperatures represented as T_1 for a first layer area, T_2 for a second layer area etc. from the side of said metal, satisfying a relation $T_1 < T_n$ between said first forming temperature and at least a forming temperature T_n for the second or subsequent layer.

Still another object of the present invention is to provide a method for producing a photovoltaic device which comprises forming irregular surface texture in said transparent layer by, after the deposition of a layer area which is to be given said irregular surface texture, immersing the surface of said layer area in acid, alkali or aqueous salt solution.

Still another object of the present invention is to provide a method for producing a photovoltaic device wherein said acid is acetic acid, sulfuric acid, hydrochloric acid, nitric acid or perchloric acid, said alkali is sodium hydroxide, potassium hydroxide or aluminum hydroxide, and said salt is iron chloride or aluminum chloride.

Still another object of the present invention is to provide a secondary battery wherein a photovoltaic device is provided on the battery tank and an inverse current blocking diode is connected to at least an electrode of said photoelectric conversion layer.

Still another object of the present invention is to provide an artificial satellite comprising a photovoltaic device formed on a windable substrate, a rotary shaft for winding said photovoltaic device, and a power source for driving said rotary shaft.

Still another object of the present invention is to provide a roofing material comprising a corrugated plate, at least a photovoltaic device formed on said corrugated plate, a conductive sheet and a resin, wherein electric connection is made by said conductive sheet at least between said photovoltaic devices and a surface of said photovoltaic device, opposite to said corrugated plate, is covered by said resin.

Still another object of the present invention is to provide a photovoltaic device module comprising a plurality of photovoltaic devices and current-collecting electrodes, wherein serial connections of said photovoltaic devices have mutually equal light-receiving areas and the density of said current-collecting electrodes is elevated in case said photovoltaic devices are serially connected long.

Still another object of the present invention is to provide said photovoltaic device module wherein the thickness of the transparent electrode constituting said photovoltaic devices is varied.

Still another object of the present invention is to provide an automobile comprising a photovoltaic device module provided on a rear quarter pillar.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic cross-sectional view of an embodiment of the photovoltaic device of the present invention, wherein the transparent layer is composed of a first layer area only;

Fig. 2 is a schematic cross-sectional view of an embodiment of the photovoltaic device of the present invention, wherein a first layer area has irregular texture;

Fig. 3 is a schematic cross-sectional view of an embodiment of the photovoltaic device of the present invention, wherein a second layer area has irregular texture;

Figs. 4A and 4B are charts showing the effect of ZnO on reflectance at the interface between silicon and metal, in the absence Fig. 4A or presence Fig. 4B of ZnO;

Fig. 5 is a chart showing the improvement in spectral sensitivity of a photovoltaic device by irregular surface texture;

Fig. 6 is a schematic cross-sectional view of a sputtering apparatus, adapted for producing the rear reflective layer of the present invention;

Fig. 7 is a view of a sputtering apparatus adapted for producing a rear reflective layer in case the transparent layer of the present invention consists solely of a first layer area;

Fig. 8 is a schematic cross-sectional view of a sputtering apparatus adapted for producing a rear reflective layer, in case the first layer area of the present invention has irregular surface texture;

Fig. 9 is a schematic cross-sectional view of a sputtering apparatus adapted for producing a rear reflective layer, in case the second layer area of the present invention has irregular surface texture;

Fig. 10 is a schematic cross-sectional view of another embodiment of the photovoltaic device of the present invention, wherein the transparent layer is composed of a first layer area only;

Fig. 11 is a schematic cross-sectional view of another embodiment of the photovoltaic device of the present invention, wherein a first layer area has irregular texture;

Fig. 12 is a schematic cross-sectional view of another embodiment of the photovoltaic device of the present invention, wherein a second layer area has irregular texture;

Fig. 13A and 13B are a schematic view and a schematic exploded view of a photovoltaic device of the present invention, applied to a secondary battery;

Fig. 14 is an equivalent circuit diagram of an application of the secondary battery, utilizing the photovoltaic device of the present invention;

Fig. 15 is a schematic view of a connecting part of a solar cell for an artificial satellite, utilizing the photovoltaic device of the present invention;

Fig. 16 is a schematic view of an artificial satellite employing the photovoltaic device of the present invention;

Fig. 17 is a schematic magnified view of a corrugated roofing material employing the photovoltaic device of the present invention;

Fig. 18 is a schematic view of a corrugated roofing material employing the photovoltaic device of the present invention;

Fig. 19 is a schematic view of a solar cell module employing the photovoltaic device of the present invention and having a current-collecting electrode density, variable according to the area of devices;

Fig. 20 is a schematic view of an automobile utilizing the photovoltaic device of the present invention; and

Fig. 21 is an equivalent circuit diagram of an application of the photovoltaic device of the present invention in an automobile.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention has been attained in consideration of the foregoing, and is to provide a photovoltaic device of a high conversion efficiency and high reliability through the use of an improved rear reflective layer and a method for producing the same, and also is to provide a secondary battery, an artificial satellite, a roofing material, a solar cell module, an automobile or the like utilizing said photovoltaic device.

The present inventors have found that the conventional rear reflective layer has been associated with the following drawbacks:

(1) Loss of reflectance due to irregular texture of metal layer:

On the metal surface with the irregular structure, the light is randomly reflected in various directions. However, measurement with a reflectance measuring apparatus equipped with an integrating sphere capable of collecting the reflected light in all the directions indicates that the metal layer with irregular surface structure shows a considerable loss in reflectance, in comparison with the smooth metal layer. This tendency is particularly conspicuous in Al or Cu. For this reason it is not possible to effectively return the light, transmitted by the semiconductor layer, to said semiconductor layer, and the conversion efficiency of the photovoltaic does not reach, therefore, the expected level;

(2) Metal diffusion to the transparent layer surface:

The deposition of the semiconductor layer on the rear reflective layer is usually conducted with a substrate temperature of 200°C or higher. At such temperature, the metal atoms penetrate the transparent layer and diffuse to the surface thereof. Such direct contact of the metal with the semiconductor layer results in insufficient function of the transparent layer, leading eventually to lowered reliability;

(3) Metal diffusion to the semiconductor layer:

In the formation of the transparent layer, the underlying metal layer may be locally exposed. Such phenomenon is encountered particularly when the irregular texture of the metal layer is enlarged and the transparent layer is made thinner. If the semiconductor layer is deposited thereon, the metal atoms diffuse from the exposed area of the metal layer to the semiconductor layer, thus affecting the properties of the semiconductor junction;

(4) Drawbacks in the subsequent steps;

The semiconductor layer contains defects such as pinholes, through which direct contact can be formed between the electrode on the semiconductor layer and the transparent layer. Excessive current will result in such directly contacting portions, unless the transparent layer has a suitable resistance.

Also if the metal layer has an exposed portion as mentioned in (3), there may result direct contact between the upper electrode and the rear electrode through defects, such as pinholes, of the semiconductor

layer.

Through the investigation of these drawbacks, the present inventors have reached the basic concept of the present invention, to be explained in the following.

There is provided a photovoltaic device comprising a metal layer having at least a substantially smooth surface for reflecting light, a transparent layer provided on said surface and having an irregular surface at a side opposite to said smooth surface, a photoelectric conversion layer consisting of a semiconductor and provided on said transparent layer, and a transparent electrode layer provided on said photoelectric conversion layer, wherein said transparent layer is composed of plural layer areas, and a layer area provided in contact with said metal layer has an irregular surface at the side of said photoelectric conversion layer.

Also there is provided a photovoltaic device wherein said transparent layer is composed of plural layer areas in which a layer area provided in contact with said metal layer has a substantially smooth surface at the side of said photoelectric conversion layer and at least another of said layer areas has an irregular surface at the side of said photoelectric conversion layer.

Fig. 1 shows an example of the configuration of the photovoltaic device of the present invention. On a conductive substrate 101, there is formed a metal layer 102 of a high reflectance. The metal layer 102 may be dispensed with if the substrate itself is composed of a material of a sufficiently high reflectance.

At least the surface of the metal layer 102 is a smooth surface of a level not affecting the specific reflectance of the metal itself, namely of a magnitude of irregularity not exceeding 1000 Å. A transparent layer 103 is formed thereon. It is transparent to the light transmitted by the photoelectric conversion layer, has a suitable electric resistance and has an irregular surface structure. In case the transparent layer contains plural layer areas (Fig. 2 showing an example in which the transparent layer has a two-layered structure composed of a first layer area 103a and a second layer area 103b), the surface of the first layer area 103a has an irregular surface structure with a magnitude of irregularity of 500 - 20000 Å and a pitch of irregularity of 3000 - 20000 Å. The second layer area 103b formed thereon may have a considerably higher specific resistivity than in the first layer area 103a. In such case, however, the second layer area 103b has to be as thin as possible, in order to reduce the resistance per unit area of the photovoltaic device. In case the transparent layer is composed of plural layer areas (Fig. 3 showing an example with two-layered structure composed of a first layer area 103c and a second layer area 103d) wherein the first layer area 103c has a smooth light-receiving surface with a pitch of irregularity not exceeding 3000 Å and has a suitable electrical resistance while the second layer area 103d is subjected, for the formation of surface irregularity, to the action of aqueous solution of acid, alkali or salt as will be explained later, there is employed a first layer area 103c less eroded by said aqueous solution than the second layer area 103d. The second layer area 103d has an irregular surface structure with a pitch of irregularity of 3000 - 20000 Å and a height of irregularity of 500 - 20000 Å, and has light transmission characteristics and electrical properties similar to those of the first layer area.

Said transparent layer also has chemical resistance to the etchant or the like to be employed in the subsequent steps. A semiconductor junction 104 is provided thereon. As an example of the semiconductor junction, there is illustrated a PIN a-Si photovoltaic device, consisting of an n-type a-Si layer 105, an i-type a-Si layer 106 and a p-type a-Si layer 107. If the semiconductor junction layer 104 is thin, the entire layer often assumes an irregular structure similar to that of the transparent layer 103, as illustrated in Figs. 1, 2 and 3. A surface transparent electrode 108 is formed thereon, and a comb-shaped current-collecting electrode 109 is provided thereon. The above-mentioned configuration provides the following advantages:

(1) Because the surface of the metal layer 102 (or the substrate 101 itself) is smooth, the light reflectance on the metal surface is elevated. Besides, the irregular surface structure of the transparent layer 103 (and of the semiconductor junction layer 104) induces light scattering, due to the phase difference at the peaks and bottoms of the irregularity, at the interface with said transparent layer, thereby causing a light trapping effect inside the semiconductor junction layer 104. For this reason the incident light is effectively absorbed, and the conversion efficiency of the photovoltaic device is improved.

(2) The smooth surface of the metal layer 102 (or the substrate 101 itself) reduces the contact area with the transparent layer 103, thereby reducing the diffusion of the metal atoms into the transparent layer 103.

Also since the transparent layer 103 has an appropriate electrical resistance, an excessive current is not generated even if the photoelectric conversion layer 104 develops defects. Also as the transparent layer 103 is chemically resistant, the rear reflective layer is damaged less in the subsequent process;

(3) Even if the metal layer 102 is partially exposed in the formation of the irregular surface structure on the first layer area 103a, the probability of contact between the upper electrode and the metal layer 102 is drastically reduced because of the covering by the second layer area 103b, whereby the reliability of the photovoltaic device is significantly improved.

(4) Also since the smooth first layer area 103c is deposited on the smooth metal layer 102, the frequency of partial exposure of the metal layer 102, that can be encountered when the metal layer is given the irregular surface structure, is extremely reduced, whereby the diffusion of the metal atoms from the metal layer 102 to the semiconductor layer 104 can be prevented:

(5) Also since the smooth first layer area 103c is deposited on the smooth metal layer 102, the frequency of partial exposure of the metal layer 102, that can be encountered when the metal layer is given the irregular surface structure, is extremely reduced, whereby obtained is a photovoltaic device of high reliability, with scarce contact between the upper electrode and the metal layer.

In the following there will be explained experiments for verifying the effects of the present invention.

[Experiment 1]

On a 5 x 5 cm stainless steel plate (SUB 430), Al was deposited with a thickness of 1500 Å by DC magnetron sputtering, with the substrate at the room temperature. Then ZnO was deposited with a thickness of 4000 Å by DC magnetron sputtering, with a substrate temperature of 250 °C. In the SEM observation, the Al surface was smooth and lustrous, while the ZnO surface was turbid, showing concentrated crater-shaped recesses with diameters in a range of 4000 - 6000 Å. In this state the light reflectance was measured within a wavelength range of 6000 - 9000 Å. On thus formed rear reflective layer, there was formed a semiconductor junction layer, by depositing, by means of glow discharge decomposition, an n-type a-Si layer of a thickness of 200 Å utilizing SiH₄ and PH₃ as the raw material gasses, an i-type a-Si layer of a thickness of 4000 Å utilizing SiH₄ as the raw material gas, and a p-type microcrystalline (μc) Si layer of a thickness of 100 Å utilizing SiH₄, BF₃ and H₂ as the raw material gasses. (Amorphous silicon obtained by glow discharge decomposition of SiH₄ etc. is generally written as a-Si:H because it contains hydrogen in about 10%, but, in the present text, it is represented as a-Si for the purpose of simplicity.) An ITO film of a thickness of 650 Å was deposited thereon by resistance-heated deposition, and a current-collecting electrode of a width of 300 microns was formed thereon by silver paste, thereby obtaining a sample 1a.

A sample 1b was prepared in the identical manner as the sample 1a, except that the Al deposition was conducted with a substrate temperature of 300 °C.

Also a sample 1c was prepared in the identical manner as the sample 1a, except that the ZnO was conducted with the substrate at the room temperature.

Also a sample 1d was prepared in the identical manner as the sample 1a, except that the stainless steel substrate was employed without deposition of Al or ZnO.

Also a sample 1e was prepared in the identical manner as the sample 1a, except that the stainless steel substrate was replaced by an Al substrate of a same size, of which surface was polished to a pitch of irregularity of about 1000 Å and that the Al deposition was not conducted.

Five samples thus obtained were subjected to the measurement of the conversion efficiency as the photoelectric conversion devices, in a solar simulator of AM-1.5. The obtained results are shown in Table I, from which following conclusions can be deduced:

(1) The conversion efficiency can be improved with any rear reflective layer, in comparison with the case of absence of the rear reflective layer;

(2) The highest efficiency in the rear reflective layer is obtained when the Al layer had a smooth surface and the ZnO layer had an irregular surface texture; and

(3) The polished Al substrate has an equivalent effect as the smooth Al layer formation.

[Experiment 2]

A sample 2a was obtained in the same manner as the sample 1a in the experiment 1, except that Al was replaced by Ag and that the current-collecting electrode was not formed.

Also a sample 2b was prepared in the same manner as the sample 2a, except that the Ag deposition was conducted with a substrate temperature of 350 °C instead of the room temperature.

In the sample 2a, the entire rear reflective layer lacked lustre because the ZnO layer had an irregular surface structure although the Ag surface was smooth. In the sample 2b, the Ag surface had irregular structure.

Table 2 shows the results of measurement of the conversion efficiency of both samples in a solar simulator of AM-1.5. The sample 2b showed a very low conversion efficiency, which is attributed to a shortcircuiting, in consideration of the current-voltage characteristics. Also in the SEM observation of both samples, the sample 2b showed scattered spot-shaped defects, and Auger analysis of these defect locations indicated Ag diffusion to the surface.

[Experiment 3]

A sample 3a was prepared in the same manner as the sample 1a in the experiment I, except that a-Si deposition was conducted in a deposition chamber which had been used for film deposition for a prolonged period without chamber cleaning.

Also a sample 3b was prepared in the same manner as the sample 3a, except that the ZnO deposition was conducted with a ZnO target containing 0.5% of Cu.

Table 3 shows the results of measurement of the conversion efficiency of both samples in a solar simulator of AM-1.5. Both samples showed lower conversion efficiencies than in the sample 1a, under the influence of shortcircuiting, particularly conspicuous in the sample 3a. In the SEM observation, both samples showed a lot of pinholes in the a-Si layer. For reference, the resistivity of ZnO, measured by forming a chromium (Cr) electrode directly on the surface of the rear reflective layer and giving a weak current, was $5 \times 10^2 \Omega\text{cm}$ in the sample 3a and $2 \times 10^5 \Omega\text{cm}$ in the sample 3b. It is therefore considered that, in the sample 3b, the specific resistivity of ZnO was suitably elevated, thereby suppressing the current in the pinholes.

[Experiment 4]

A sample 4a was prepared in the same manner as the rear reflective layer of the sample 1a in the experiment I, except that the ZnO deposition was conducted with a ZnO target containing 0.5% of Cu. Also the rear reflective layer of the sample 1a was taken as a sample 4b. Both samples were immersed, for 5 minutes, in 30% aqueous solution of ferric chloride, which is the etchant employed for ITO patterning. The sample 4a did not show any particular change, but, in the sample 4b, ZnO was significantly corroded. From these results it is expected that the rear reflective layer of the sample 4a is less prone to be damaged in the subsequent steps, even if the thin semiconductor films have defects such as pinholes.

[Experiment 5]

A sample 5 was prepared in the same manner as the sample 1a in the experiment I, except that the deposition of i-type a-Si layer was conducted with a triple power of glow discharge and with a 1/3 flow rate of SiH_4 , combined with the depositing conditions so regulated as to obtain a film thickness of 4000 Å. The SEM observation of the samples 1a, 5 and of the rear reflective layers employed thereon provided following results. The surface of the sample 1a showed concentrated crater-shaped recesses with diameters of 4000 - 6000 Å as on the surface of the rear reflective layer, with almost same depth of craters on both surfaces. On the other hand, the surface of the sample 5 showed heaved structures of a pitch finer than the recesses on the rear reflective layer, apparently indicating an aspect different from the structure of the rear reflective layer.

In an evaluation in the solar simulator, the sample 5 showed a conversion efficiency of 8.2%, lower than that of the sample 1a. This difference is principally due to a low shortcircuit photocurrent, indicating an insufficient phototrapping effect in case, as in the sample 5, the surface structure of the semiconductor layer is different from that of the rear reflective layer.

[Experiment 6]

On a 5 x 5 cm stainless steel plate (SUS 430), Al was deposited with a thickness of 1500 Å by DC magnetron sputtering, with the substrate at the room temperature. Then ZnO was deposited thereon with a thickness of 4000 Å by magnetron sputtering, with a substrate temperature of 300 °C. In SEM observation, the Al surface was lustrous and smooth with a pitch of irregularity of 1000 Å or less, while the ZnO surface was turbid, with concentrated crater-shaped recesses of diameters of 4000 - 9000 Å.

The height of irregularity was about 2000 - 4000 Å. ZnO was further deposited thereon with a thickness of 500 Å, by magnetron sputtering with the substrate at the room temperature. In SEM observation, this layer maintained an irregular surface structure similar to that of the first layer area formed with the substrate temperature of 300 °C. In this state the light reflectance was measured in a wavelength range of 6000 - 9000 Å. Subsequently there were formed a semiconductor junction, a transparent electrode and a current-collecting electrode to obtain a sample 6a.

Also a sample 6b was prepared in the same manner as the sample 6a, except that the Al deposition was conducted with a substrate temperature of 100 °C.

Also a sample 6c was prepared in the same manner as the sample 6a, except that the ZnO of the second layer area (at the side of the semiconductor layer) was not deposited.

Also a sample 6d was prepared in the same manner as the sample 6a, except that ZnO of the first layer area was deposited with a thickness of 4500 Å with a substrate temperature of 300 °C, and that ZnO of the second layer area was not deposited.

Also a sample 6e was prepared in the same manner as the sample 6a, except that ZnO of the first layer area was deposited with a thickness of 4000 Å with the substrate at the room temperature, and that ZnO of the second layer area was not deposited.

Also a sample 6f was prepared in the same manner as the sample 6a, except that ZnO of the first layer area was deposited with a thickness of 4500 Å with the substrate at the room temperature, and that ZnO of the second layer area was not deposited.

Also a sample 6g was prepared in the same manner as the sample 6a, except that the stainless steel substrate was replaced by an Al substrate of a same size; of which surface was polished to a pitch of irregularity of about 1000 Å.

Seven samples thus prepared were subjected to the measurement of the conversion efficiency of solar cells, as an example of the photovoltaic device, in a solar simulator of AM-1.5. The obtained results are shown in Table 4, from which following conclusions are deduced:

(1) The conversion efficiency was improved when a smooth metal layer (pitch of irregularity not exceeding 1000 Å) is combined with a transparent layer with an irregular surface structure (samples 6a, 6c, 6d and 6g);

(2) The samples 6a, 6c, 6d and 6g were substantially same in the conversion efficiency, but the one-layered transparent layer (6c, 6d) and the two-layered transparent layer (6a, 6g) respectively provided yields of photovoltaic devices of about 70% and about 95%, with apparently improved reliability in the two-layered structure (said yield being calculated by the shunt resistance per unit area (1 cm²), determined from the measurement of the current-voltage characteristics of each sample, each sample being rated as acceptable if said shunt resistance is equal to 200 Ωcm or higher and not acceptable below 200 Ωcm).

This difference is presumably due to the following phenomena. In the one-layered structure, in the formation of irregular structure in the transparent layer, the recesses locally grew larger, thus partially exposing the metal layer and causing electrical short-circuiting through such exposed areas when the photovoltaic device is formed. On the other hand, in the two-layered structure, said exposed areas are effectively covered by the second layer area, whereby the frequency of the shortcircuiting is reduced and the yield is increased.

[Experiment 7]

A sample 7a was prepared in the same manner as the sample 6a in the experiment 6, except that ZnO of the first layer area was deposited with a thickness of 10000 Å and that the substrate was thereafter immersed in 10% aqueous solution of acetic acid for 1 minute at the room temperature.

Also a sample 7b was prepared in the same manner as the sample 7a except that ZnO of the first layer areas had a thickness of 25000 Å.

Also a sample 7c was prepared in the same manner as the sample 7b, except that the immersion of the substrate in 10% aqueous acetic acid solution was conducted for 90 seconds. Also a sample 7d was prepared in the same manner as the sample 7b, except that the immersion of the substrate in 10% aqueous acetic acid solution was conducted for 3 minutes.

SEM observation showed that the magnitude of the irregular structure of the first layer area of ZnO transparent layer grew with the immersion time, due to the eroding action of the acetic acid solution.

In SEM observation, the samples 7a and 7d showed locally exposed areas of the metal layer immediately after immersion in the acetic acid solution, but such local exposures of the metal layer could no longer be observed after the deposition of the second layer area of the ZnO transparent layer. Table 5 shows the results of measurement of the conversion efficiency of four samples under AM-1.5. The samples 7a, 7b and 7c showed high conversion efficiencies but the sample 7d did not show such high conversion efficiency.

[Experiment 8]

A sample 8a was prepared in the same manner as the sample 6a, except that the deposition of the transparent layer was not conducted at all in the experiment 6.

Under AM-1.5, the sample 8a shows a conversion efficiency of 2.2%. Auger microanalysis of the a-Si layer of said sample 8a detected aluminum atoms.

It was therefore confirmed that the direct contact between the metal layer and the semiconductor layer induced diffusion of metal atoms into the semiconductor layer.

[Experiment 9]

On a 5 x 5 cm stainless steel substrate (SUB 430), Al was deposited with a thickness of 1500 Å by DC magnetron sputtering, with the substrate at the room temperature. Then ZnO was deposited with a thickness of 1000 Å by DC magnetron sputtering, also with the substrate at the room temperature. In SEM observation, the Al surface was a lustrous smooth surface with a pitch of irregularity of 1000 Å or less. Also the ZnO layer had a lustrous smooth surface, though yellowish, with a pitch of irregularity of 1000 Å or less. Then ZnO was deposited thereon with a thickness of 3000 Å by DC magnetron sputtering, with a substrate temperature of 300 °C. In SEM observation, the ZnO film constituting the second layer area has a turbid surface, with a pitch of irregularity of 4000 - 8000 Å and a magnitude of irregularity of 2000 - 3000 Å. In this state, the light reflectance was measured in a wavelength range of 6000 - 9000 Å.

Subsequently there were formed a semiconductor junction, a transparent electrode and a current-collecting electrode in the same manner as in the experiment 1, whereby a sample 9a was obtained.

Also a sample 9b was prepared in the same manner as the sample 9a, except that the Al deposition was conducted with a substrate temperature of 100 °C.

Also a sample 9c was prepared in the same manner as the sample 9a, except that ZnO of the second layer area was not deposited.

Also a sample 9d was prepared in the same manner as the sample 9a, except that ZnO of the first layer area was deposited with a thickness of 4000 Å with the substrate at the room temperature and that ZnO of the second layer area was not deposited.

Also a sample 9e was prepared in the same manner as the sample 9a, except that ZnO of the first layer area was deposited with a thickness of 4000 Å with a substrate temperature of 300 °C and that ZnO of the second layer area was not deposited.

Also a sample 9f was prepared in the same manner as the sample 9a, except that the stainless steel substrate was replaced by an Al substrate of a same size, of which surface was polished to a pitch of irregularity of 1000 Å or less, and that Al deposition was not conducted.

Six samples thus obtained were subjected to the measurement of conversion efficiency of the solar cells, as an example of the photovoltaic device, in a solar simulator of AM-1.5. The obtained results are shown in Table 6, from which following conclusions were deduced:

(1) The conversion efficiency was improved in the use of a rear reflective layer, composed of a combination of a smooth metal layer and a transparent layer with irregular surface structure (samples 9a, 9e and 9f);

(2) Although the samples 9a, 9e and 9f were almost same in the conversion efficiency, the one-layered transparent layer (sample 9e) provided a yield of the photovoltaic devices of about 70% while the samples 9a and 9f with the two-layered transparent layer respectively provided yields of about 95%. Thus the two-layered structure was apparently higher in the yield and in the reliability. (Said yield was calculated by the shunt resistance per unit area (1 cm²), determined from the measurement of the current-voltage characteristics of each sample, and each sample was rated as acceptable if said shunt resistance is equal to 200 Ωcm and not acceptable below 200 Ωcm.) This difference is presumably due to the following phenomena. In the one-layered structure, in the formation of irregular structure in the transparent layer, the recesses locally grew larger, thus partially exposing the metal layer and causing electrical shortcircuiting between thus exposed areas and the upper electrode, through defects such as pinholes in the semiconductor layer formed thereon. On the other hand, the use of a two-layered transparent layer in which the first layer area has a smooth surface drastically reduces the formation of said exposed areas, thereby reducing the rate of formation of electrical shortcircuitings and improving the yield.

[Experiment 10]

A sample 10a was prepared in the same manner as the sample 9a, except that Al in the experiment 9 was replaced by Ag and the current-collecting electrode was not formed:

Also a sample 10b was prepared in the same manner as the sample 10a, except that the Ag deposition was conducted with a substrate temperature of 300 °C instead of the room temperature.

In the sample 10a, the rear reflective layer lacked lustre, because ZnO had irregular surface structure though Ag had a smooth surface. In the sample 10b, the Ag surface showed an irregular structure.

Table 7 shows the result of measurement of the conversion efficiency under AM-1.5 of both samples. The sample 10b showed a significantly low conversion efficiency, presumably due to shortcircuiting, based on the current-voltage characteristics. In SEM observation of both samples, the sample 10b showed scattered spot-shaped defects, and Auger analysis of these defects revealed Ag diffusion to the surface.

[Experiment II]

In the process of the experiment 9, SnO_2 was deposited, as the first layer area, with a thickness of 1000 Å by DC magnetron sputtering, with a substrate temperature of 200 °C. The SnO_2 showed a lustrous smooth surface, with a pitch of irregularity not exceeding 1000 Å. Then ZnO was deposited thereon, as the second layer area, with a thickness of 10000 Å, with a substrate temperature of 300 °C. A sample 11a was obtained by a subsequent process same as that in the sample 9a, except that the substrate surface was immersed in 20% aqueous solution of perchloric acid for 30 seconds at room temperature.

Also a sample 11b was obtained in the same manner as the sample 11a, except that the immersion of the substrate surface in 20% aqueous solution of perchloric acid was conducted for 45 seconds.

Also a sample 11c was prepared in the same manner as the sample 11a, except that ZnO of the second layer area was deposited with a thickness of 25000 Å.

Also a sample 11d was prepared in the same manner as the sample 11c, except that the immersion of the substrate surface in 20% aqueous solution of perchloric acid was conducted for 45 seconds.

Also a sample 11e was prepared in the same manner as the sample 11c, except that the immersion of the substrate surface in 20% aqueous solution of perchloric acid was conducted for 90 seconds.

SEM observation showed that the irregularity of the irregular surface structure of ZnO constituting the second layer area grew larger with the immersion time, by the corroding action of the aqueous perchloric acid solution.

In comparison with the irregularity of the sample 11d, that of the sample 11b is smaller. This is presumably due to the weaker action of the aqueous perchloric acid solution to SnO_2 than to ZnO.

Table 8 shows the result of measurement of the conversion efficiency of these five samples under AM-1.5. Although the samples 11a to 11d showed high conversion efficiencies, the sample 11e did not show a high conversion efficiency.

In the following there will be given a detailed explanation on the rear reflective layer to be employed in the photovoltaic device of the present invention.

[Substrate and metal layer]

Various metals can be employed as the substrate. In particularly stainless steel plate, zincated steel plate, aluminum plate and copper plate are preferred because of the relatively low cost. Such metal plate may be cut into a predetermined shape, or may be employed as a continuous web, depending on the thickness. The latter form, being windable into a coil, is suitable for continuous production, and facilitates storage and transportation. Also for certain applications there may be employed a crystalline substrate such as of silicon, or a plate of glass or ceramics. The substrate surface may be polished, or it may be used without polishing in case the surface finish is satisfactory as in bright annealed stainless steel plate.

A substrate with a low light reflectance such as stainless steel plate or zincated steel plate, or a substrate with a low conductivity such as glass or ceramic plate can be used as the substrate of the present invention, by forming thereon a metal layer of a high reflectance such as of silver, aluminum or copper. However, since the shorter wavelength component in the solar light spectrum is already absorbed by the semiconductor layer, the rear reflective layer needs only to have a high reflectance to the light of the longer wavelength region. The shortest boundary wavelength of such high reflectance region depends on the optical absorption coefficient and the thickness of the semiconductor material to be employed. As an example, in case of a-Si with a thickness of 4000 Å, said boundary wavelength is about 6000 Å, so that copper can be advantageously used.

The metal layer deposition, it employed, can be achieved, for example, by vacuum evaporation by resistance heating or with electron beam, sputtering, ion plating, CVD or plating. Sputtering will be explained in the following, as an example of film forming method. Fig. 6 shows an example of the sputtering apparatus, in which a deposition chamber 401 can be evacuated by an unrepresented vacuum pump. Inert gas such as argon (Ar) is introduced into said chamber, with a predetermined flow rate from a gas supply pipe 402 connected to an unrepresented gas container, and the interior of the deposition chamber 401 is

maintained at a predetermined pressure by the adjustment of the aperture of an exhaust valve 403. A substrate 404 is fixed on an anode 406, containing a heater 405 therein. Opposed to the anode 406 there is provided a cathode 408, supporting thereon a target 407, which is a block of the metal to be deposited. It is usually composed of the metal of a purity of 99.9 to 99.999%, but specific impurity may be contained in certain cases. The cathode is connected to a power source 409, which applies an RF (radio frequency) or DC high voltage, thereby generating plasma 410 between the cathode and the anode. The metal atoms of the target 407 are deposited onto the substrate 404, by the action of said plasma. A higher deposition rate can be obtained in a magnetron sputtering apparatus in which a magnet is provided in the cathode 408 for increasing the plasma intensity.

An example of the depositing conditions is as follows. There were employed an Al target of a purity of 99.99% and a diameter of 6 inches; a substrate consisting of stainless steel plate (SUS 430) of a size of 5 x 5 cm and a thickness of 1 mm, with polished surface; a distance of 5 cm between the target and the substrate; and a flow rate of Ar of 10 sccm, with a pressure of 1.5 mTorr. A DC voltage of 500 V generated plasma with a current of 2A, and the discharge was maintained in this state for 1 minute. Samples 13a, 13b, 13c and 13d were obtained respectively at substrate temperatures of room temperature, 100 °C, 200 °C and 300 °C. Table 9 summarizes the appearance and the result of SEM observation of these samples. The Al surface apparently varied from smooth surface to irregular surface, with the increase in temperature. Similar tendency is generally observed in other metals and in other film forming methods.

[Transparent Layer and its Irregular Structure]

The transparent layer is often composed of oxides such as ZnO, In_2O_3 , SnO_2 , CdO, CdSnO_3 or TiO_2 , though the actual composition ratio of these compounds does not necessarily coincide with that of the chemical formula. The optical transmittance of the transparent layer should preferably be as high as possible, but it need not be transparent to the light of the wavelength region which is absorbed by the semiconductor, or which is not at all absorbed by the semiconductor. The transparent layer should preferably have a certain electrical resistance in order to suppress the current generated for example by the pinholes, but said resistance should be such that the influence of the serial resistance loss resulting from said resistance is negligible on the conversion efficiency of the photovoltaic device. Based on these considerations, the resistance per unit area (1 cm^2) of the transparent layer should preferably within a range from 10^{-6} to 10Ω , more preferably from 10^{-5} to 3Ω , and most preferably from 10^{-4} to 1Ω . Also the thickness of the transparent layer is preferably as small as possible in consideration of the transparency, but should be 500 Å at least in consideration of multiple interference. Also average thickness should be at least 1000 Å for forming the irregular surface structure. A larger film thickness may be required in consideration of the reliability. In case of plural layer areas, an average film thickness of 1000 Å is required at least, in order to form the irregular surface structure in the first layer area.

The irregular structure can be formed in the first layer area, by elevating the temperature at the deposition of the layer in contact with the metal layer. In this case, the temperature T_1 for forming the first layer area varies suitably according to the material and apparatus employed in said formation, but is preferably higher than 200 °C in the DC magnetron sputtering employing a ZnO target (purity 99.9%). Also since the irregular surface structure of oxide or the like employed in said transparent layer grows as the forming temperature becomes higher, there is employed a relation $T_1 > T_n$ wherein T_n is the forming temperature of the n-th layer area.

An alternative method for forming the irregular structure consists, after formation of the first layer area, of immersing the surface thereof in aqueous solution of acid, alkali or salt. A desired irregular structure can be obtained by regulating the length of the immersing time. The frequently used examples of acid include acetic acid, sulfuric acid, hydrochloric acid, nitric acid and perchloric acid, while those of alkali include sodium hydroxide, potassium hydroxide and aluminum hydroxide, and those of salt include ferric chloride and aluminum chloride.

Another alternative method for forming the irregular structure consists, after formation of the first layer area, of bombarding the transparent layer on which the irregular structure is to be formed, with plasma or ions for example by inverse sputtering. This method can be conducted in a relatively simple manner, and is suitable for batch process. The second or any subsequent layer area in the transparent layer should be of such thickness that does not deteriorate the irregular structure formed by the first layer area. Further in consideration of the thickness of the semiconductor layer to be deposited thereon, said thickness is preferably within a range from 500 to 3000 Å, more preferably from 500 to 2500 Å, and most preferably from 500 to 2000 Å.

The forming temperature T_n of at least an n -th layer area among the second and subsequent layer areas should be made as low as possible, in order to form a smooth surface for completely covering the irregularity of the first layer area. Said n -th forming temperature T_n varies suitably according to the material and apparatus employed in the formation of the n -th layer area, but a condition $T_n < 200^\circ\text{C}$ is preferred for example in the DC magnetron sputtering, employing a ZnO target (purity 99.9%).

Also in another example composed of plural layer areas, the first forming temperature T_1 is preferably made as low as possible, as a method for forming a pitch of irregularity not exceeding 3000 \AA in the first layer area. Said first forming temperature T_1 varies according to the material and apparatus employed in the formation of the first layer area, but a condition $T_1 < 200^\circ\text{C}$ is preferred for example in the DC magnetron sputtering, employing a ZnO target (purity 99.9%).

Among the second and subsequent layer areas in the transparent layer, the n -th layer area having the irregular surface structure should have an average thickness of 1000 \AA or larger, in order to have such irregular structure. A method for forming said irregular structure consists of elevating the n -th forming temperature T_n . Said temperature T_n varies depending on the material and apparatus employed for the formation of the n -th layer area, but a condition $T_n > 200^\circ\text{C}$ is preferred for example in the DC magnetron sputtering, employing a ZnO target (purity 99.9%). Also since the irregular surface structure of the oxide or the like employed in said transparent layer grows larger as the forming temperature T becomes higher, there is employed a relation $T_1 < T_n$.

An alternative method for forming the irregular structure consists, after the deposition of the n -th layer area in which said irregular structure is to be formed, of immersing the surface thereof in aqueous solution of acid, alkali or salt. A desired irregular structure can be obtained by regulating the length of the immersion time. Examples of such acid include acetic acid, sulfuric acid, hydrochloric acid, nitric acid and perchloric acid, while those of said alkali include sodium hydroxide, potassium hydroxide and aluminum hydroxide, and those of said salt include ferric chloride and aluminum chloride.

Another alternative method for forming the irregular structure consists, after the deposition of a transparent layer area in which the irregular structure is to be formed, of bombarding the surface thereof with plasma or ions for example by sputtering. This method can be relatively easily conducted, and is suitable for a batch process.

Among the second and subsequent layer areas in the transparent layer, the n -th layer area having said irregular structure and the subsequent layer areas deposited thereon should have a total thickness not deteriorating said irregular structure. Also in consideration of the thickness of the semiconductor to be provided thereon, said total thickness is preferably within a range from 500 to 3000 \AA , more preferably from 500 to 2500 \AA , and most preferably from 500 to 2000 \AA .

The transparent layer may be deposited by vacuum evaporation employing resistance heating or an electron beam, sputtering, ion plating, CVD or spray coating. The sputtering method will be explained as an example of the film forming method. Also in this case the sputtering apparatus shown in Fig. 6 may be employed. In case of oxide deposition, however, there may be employed a target of oxide itself or of a metal (Zn, Sn etc.). In the latter case, oxygen has to be supplied, together with argon, to the deposition chamber (called reactive sputtering).

In the following there are shown examples of the conditions for deposition and irregular structure formation. There was employed a stainless steel plate (SUS 430) of a size of $5 \times 5\text{ cm}$ and a thickness of 1 mm , with a polished surface, as the substrate. There was also employed a ZnO target of a diameter of 6 inches , with a purity of 99.9% , at a distance of 5 cm between the target and the substrate. Argon was supplied with a flow rate of 10 sccm and maintained at a pressure of 1.5 mTorr , and a DC voltage of 500 v was applied to generate plasma, with a current of 1 A . The discharge was maintained in this state for 5 minutes . Samples 14a, 14b, 14c and 14d were obtained respectively maintaining the substrate at room temperature, 100°C , 200°C and 300°C . Table 10 summarizes the appearances and the results of SEM observation of these samples. The surface state of ZnO varied as the temperature was elevated. The turbid samples 14c and 14d showed crater-shaped recesses on the surface, which are assumed to be the cause of turbidity.

In the following there are shown examples of the conditions for deposition and irregular structure formation, in case of plural layer areas in which the first layer area has an irregular surface structure.

There were employed same conditions as above, except that the discharge was continued for 15 minutes . Samples 15a, 15b, 15c and 15d were prepared by maintaining the substrate at the room temperature, 100°C , 200°C and 300°C respectively. The surface state of ZnO varied as the temperature was elevated. The turbid samples 15c and 15d showed crater-shaped recesses on the surface, which were considered as the cause of turbidity. Additionally samples 15e and 15f were prepared by immersing the sample, prepared at the substrate temperature of 200°C , in 10% aqueous solution of acetic acid,

respectively for 1 and 1.5 minutes. Table 11 summarizes the appearances and the result of SEM observation of these samples.

The samples 15a - 15f thus prepared were again subjected to the deposition of ZnO by sputtering under same conditions as above but with a discharge time of 1.5 minutes, whereby obtained was a deposition film of an irregular surface structure substantially same as that of the samples 15a - 15f.

In the following there are shown examples of the conditions for deposition and irregular structure formation, in case of plural layer areas in which at least one in the second and subsequent layer areas has an irregular surface structure.

There were employed same conditions as above, except that the discharge was continued for 1.5 minutes, with the substrate at the room temperature.

Then ZnO of the second layer area was deposited by similar sputtering, with a discharge time of 15 minutes. Samples 16a, 16b, 16c and 16d were prepared by respectively maintaining the substrate at the room temperature, 100°C, 200°C and 300°C. Table 12 summarizes the appearances and the result of SEM observation of these samples.

The light trapping can be attributed to the light scattering in the metal layer in case the metal layer itself has the irregular structure, but to the scattering by aberration of the light phase between the peaks and bottoms of the irregularity at the semiconductor surface and/or the interface between the semiconductor and the transparent layer, in case the metal layer is smooth and the transparent layer has the irregular surface structure. The pitch of irregularity is preferably in a range from 3000 to 20000 Å, more preferably from 4000 to 15000 Å, and the height of irregularity is preferably in a range of 500 to 20000 Å, more preferably from 700 to 10000 Å. When the semiconductor surface has an irregular structure similar to that of the transparent layer, there is facilitated the scattering by the phase difference, so that the light trapping effect is enhanced.

For controlling the specific resistivity of the transparent layer, there is preferably added a suitable impurity. In the transparent layer of the present invention, the resistance should preferably be suitably elevated by the addition of an impurity since the aforementioned conductive oxides may have excessively low specific resistivities, and also for reducing the entire thickness. For example an n-type semiconductor may be added with an acceptor-type impurity (such as Cu to ZnO or Al to SnO₂) of a suitable amount, for achieving the intrinsic character and elevating the resistance.

In case the transparent layer is composed of plural layer areas, suitable impurities may be added respectively to said layer areas but a suitable resistance in the entire transparent layer may be obtained by introducing the impurity in at least a layer area.

Also such intrinsic transparent layer generally becomes more resistant to the etching by acid or alkali. There are therefore obtained additional advantages that it is less attacked by the chemicals employed in the patterning of the semiconductor layer or the ITO layer in the subsequent steps of manufacture of the photovoltaic devices, and that the durability of the photovoltaic device is improved in the prolonged use under high temperature and high humidity.

However, such intrinsic state of the transparent layer is undesirable as it deteriorates the work efficiency, if etching with aqueous solution of acid, alkali or salt is employed for the formation of the irregular surface structure of the transparent layer. In such case, a photovoltaic device of a suitable resistance, with high chemical resistance and high durability, can be obtained by etching the transparent layer without impurity introduction and by then laminating another transparent layer of intrinsic state. The impurity addition to the transparent layer may be achieved by adding the desired impurity in the evaporation source or the target as explained in the experiments 3 and 4, or, in case of sputtering, by placing a small piece of a material containing the impurity.

[Embodiment 1]

In this embodiment, there was prepared a photovoltaic device of the PIN a-Si structure shown in Fig. 1 in which, however, the metal layer 102 was absent. On an Al plate 101 of a size of 5 x 5 cm and a thickness of 1 mm, with a polished surface, a ZnO layer 103 with an average thickness of 4000 Å was deposited, in the apparatus shown in Fig. 6 employing a ZnO target containing 5 % of Cu, with a substrate temperature of 250°C. The ZnO surface showed an irregular structure.

The substrate bearing thus formed lower electrode was set in a commercial capacitance-coupled high-frequency CVD apparatus (Ulvac CHJ-3030), and the reaction chamber was evacuated coarsely and then finely through a vacuum tube connected to a vacuum pump. The surface temperature of the substrate was maintained at 250°C by a temperature control mechanism. After sufficient evacuation, SiH₄ at 300 sccm, SiF₄ at 4 sccm, PH₃/H₂ (diluted to 1 % with H₂) at 55 sccm and H₂ at 40 sccm were introduced from gas supply tubes, and the internal pressure of the reaction chamber was maintained at 1 Torr by the regulation

of a throttle valve. When the pressure was stabilized, an electric power of 200 W was applied from a high-frequency power source, and the plasma was maintained for 5 minutes. Thus an n-type a-Si layer 105 was formed on the transparent layer 103. After evacuation of the reaction chamber again, SiH₄ at 300 sccm, SiF₄ at 4 sccm and H₂ at 40 sccm were introduced from the gas supply tubes, and the internal pressure of the reaction chamber was maintained at 1 Torr by the regulation of the throttle valve. When the pressure was stabilized, an electric power of 150 W was applied from the high-frequency power source, and the plasma was maintained for 40 minutes. Thus an i-type a-Si layer 106 was formed on the n-type a-Si layer 105. After subsequent evacuation of the reaction chamber again, SiH₄ at 50 sccm, BF₃/H₂ (diluted to 1 % with H₂) at 50 sccm and H₂ at 500 sccm were introduced from the gas supply pipes, and the internal pressure of the reaction chamber was maintained at 1 Torr by the regulation of the throttle valve. When the pressure was stabilized, an electric power of 300 W was applied from the high-frequency power source, and the plasma was maintained for 2 minutes. Thus a p-type μ c-Si layer 107 was formed on the i-type a-Si layer 106. Subsequently the sample was taken out from the CVD apparatus, subjected to ITO deposition in a resistance-heated vacuum evaporation apparatus, then printing of paste containing aqueous ferric chloride solution for patterning the transparent electrode 108 into the desired shape, and screen printing of silver paste for forming a current-collecting electrode 109, whereby a photovoltaic device was completed. Ten samples were prepared in this manner and subjected to the measurement of the photoelectric conversion efficiency under the light irradiation of AM-1.5 (100 mW/cm²), whereby an excellent efficiency of 9.5 ± 0.2 % was reproducibly obtained. Also these photovoltaic devices, after standing for 1000 hours under the conditions of a temperature of 50 °C and a relative humidity of 90 %, showed a conversion efficiency of 9.2 ± 0.5 % with almost no deterioration of the efficiency.

[Embodiment 2]

In the present embodiment prepared was a PIN a-SiGe photovoltaic device of the configuration shown in Fig. 1. On a surface-polished stainless steel plate 101 of a size of 5 x 5 cm and a thickness of 1 mm, there was formed a Cu layer 102 of a thickness of 1500 Å with a smooth surface by plating. Then Zn containing 1 % of Cu was ion plated in oxygen atmosphere with a substrate temperature of 350 °C to deposit a ZnO layer of an average thickness of 1 μ with an irregular surface structure.

Ten samples were prepared by a subsequent process same as in the embodiment 1, except that the i-layer was composed of a-SiGe deposited by introducing Si₂H₆ at 50 sccm, GeH₄ at 10 sccm and H₂ at 300 sccm, maintaining the internal pressure of the reaction chamber at 1 Torr, applying an electrical power of 100 W and maintaining the plasma for 10 minutes. In the measurement under the light of AM-1.5 (100 mW/cm²), these devices showed an excellent conversion efficiency of 8.5 ± 0.3 % in a reproducible manner.

[Embodiment 3]

An apparatus shown in Fig. 7 was employed for forming the rear reflective layer in continuous manner. In a substrate feeding chamber 603, there was set a roll 601 of an already washed stainless steel sheet of a width of 350 mm, a thickness of 0.2 mm and a length of 500 m. The stainless steel sheet 602 was fed therefrom to a takeup chamber 606, through a metal layer deposition chamber 604 and a transparent layer deposition chamber 605. The sheet 602 could be heated to desired temperatures in respective deposition chambers by heaters 607, 608. The chamber 604 was equipped with a target 609 composed of Al of a purity of 99.99 %, for depositing Al onto the sheet 602 by DC magnetron sputtering. The chamber 605 was equipped with targets 610 of ZnO of a purity of 99.5 %, containing 0.5 % of Cu, for depositing a ZnO layer in succession by DC magnetron sputtering. There were provided four targets 610 in consideration of the deposition rate and the desired film thickness.

The rear reflective layer was formed with this apparatus, at a sheet feeding speed of 20 cm/min, and with a substrate temperature of 250 °C at the ZnO deposition, achieved by the heater 608 alone. Argon was supplied with a pressure of 1.5 mTorr, and a DC voltage of 500 V was applied to the cathodes. There were obtained a current of 6 A in the target 609 and a current of 4 A in each of the targets 610. On the taken-up sheet there were obtained an Al layer of a thickness of 1600 Å and a ZnO layer of a thickness of 3800 Å in average, with a turbid surface.

An a-Si/a-SiGe tandem photovoltaic device of the configuration shown in Fig. 10 was formed thereon. In Fig. 10 there are shown a substrate 701; a metal layer 702; a transparent layer 703; a bottom cell 704; a top cell 708; n-type a-Si layers 705, 709; p-type μ c-Si layers 707, 711; an i-type a-SiGe layer 706; and an i-type a-Si layer 710. These semiconductor layers were formed in continuous manner by a roll-to-roll film forming

apparatus as disclosed in the U.S. Patent No. 4,492,181. A transparent electrode 712 was formed by a sputtering apparatus similar to that shown in Fig. 7. There is also provided a current-collecting electrode 713. After the patterning of the transparent electrode and the formation of the current-collecting electrodes, the sheet 602 was cut into pieces. The mass production was achieved by conducting the entire process in continuous manner.

100 samples were prepared in this manner and evaluated under the light of AM-1.5 (100 mW/cm²). There was obtained an excellent conversion efficiency of 11.2 ± 0.2 % in reproducible manner. After standing for 1000 hours under the conditions of 50 °C in temperature and 90 % in relative humidity, the conversion efficiency was 10.8 ± 0.6 %, with almost no change. Also other 100 samples, irradiated with the light corresponding to AM-1.5 for 600 hours in open state, showed a conversion efficiency of 10.5 ± 0.3 %, indicating that the deterioration by light is also little. These results were based on the tandem structure which enabled effective absorption to the long wavelength region and attained a higher output voltage, and also based on the reduced deterioration of the semiconductor layer under light irradiation. Thus, in combination with the effect of the rear reflective layer of the present invention, there could be obtained a photovoltaic device of high reliability and a high conversion efficiency.

[Embodiment 4]

A rear reflective layer was formed in the same manner as in the embodiment 1, except that a surface-polished Cu plate was employed as the substrate. On thus treated substrate and on a substrate without ZnO deposition, Cu and In were deposited by sputtering, with respective thicknesses of 0.2 and 0.4 μ . The samples were then transferred to a quartz glass bell jar and heated to 400 °C therein, and hydrogen selenide (H₂Se) diluted to 10 % with hydrogen was supplied therein to form a thin film of CuInSe₂ (CIS). Then a CdS layer of a thickness of 0.1 μ was formed thereon by sputtering, and a p/n junction was formed by annealing at 250 °C. A transparent electrode and current-collecting electrodes were then formed thereon in the same manner as in the embodiment 1.

In the evaluation of thus obtained photovoltaic devices under the light irradiation of AM-1.5 (100 mW/cm²), the device with the ZnO layer showed an excellent conversion efficiency of 9.5 % while the device without ZnO showed an inferior efficiency of 7.3 % only. These results indicate that the present invention is effective also for the semiconductors other than a-Si.

[Embodiment 5]

In the present embodiment, there was prepared a PIN a-Si photovoltaic device of the configuration shown in Fig. 2, however without the metal layer 102. On a surface-polished Al plate 101 of a size of 5 x 5 cm and a thickness of 1mm, a ZnO layer 103a deposited with an average thickness of 4000 Å, in the apparatus shown in Fig. 6 employing a ZnO target, with a substrate temperature of 300 °C. The ZnO surface showed an irregular structure. Then, after the substrate temperature was lower to the room temperature, a ZnO layer 103b was deposited with a thickness of 500 Å.

On thus obtained rear reflective layer, a PIN a-Si semiconductor layer 104, a transparent electrode 108 and a current-collecting electrode 109 were formed in the same manner as in the embodiment 1 to complete the photovoltaic device. Ten samples were prepared in this manner and evaluated under the irradiation of AM-1.5 (100 mW/cm²). An excellent photoelectric conversion efficiency of 9.7 ± 0.2 % was reproducibly obtained. Also after standing for 1000 hours under the conditions of a temperature of 50 °C and a relative humidity of 90 %, these devices showed a conversion efficiency of 9.4 ± 0.5 %, with almost no deterioration.

[Embodiment 6]

In the present embodiment there was prepared a PIN a-SiGe photovoltaic device of the configuration shown in Fig. 2. On a surface-polished stainless steel plate 101 of a size of 5 x 5 cm and a thickness of 1 mm, a Cu layer 102 with smooth surface was formed with a thickness of 1500 Å by plating. Subsequently Zn was ion plated in oxygen atmosphere with a substrate temperature of 350 °C to deposit a ZnO layer of an average thickness of 1 μ , with an irregular surface structure. Then the substrate was immersed in 10 % aqueous acetic acid solution for 45 seconds, then dried for 20 minutes in a thermostat chamber of 80 °C, and was subjected to the deposition of a ZnO layer of a thickness of 700 Å by the above-mentioned ion plating, with the substrate at the room temperature.

Ten samples were prepared in the same subsequent process as in the embodiment 1, except that an a-SiGe layer, deposited by introducing Si_2H_6 at 50 sccm, GeH_4 at 10 sccm and H_2 at 300 sccm, maintaining the internal pressure of the reaction chamber at 1 Torr, applying an electric power of 100 W and maintaining the plasma for 10 minutes was employed as the i-type layer. In their evaluation under the irradiation of AM-1.5 (100 mW/cm²), these devices showed an excellent conversion efficiency of 8.7 ± 0.3 % in reproducible manner.

[Embodiment 7]

A rear reflective layer was continuously prepared by the apparatus shown in Fig. 8. In a feed chamber 603, a roll 601 of an already washed stainless steel sheet of a width of 350 mm, a thickness of 0.2 mm and a length of 500 m was set. The stainless steel sheet 602 was fed therefrom to a take-up chamber 606 through a metal layer deposition chamber 604, a first layer deposition chamber 605a and a second layer deposition chamber 605b. The sheet 602 could be heated to desired temperatures in said chambers by respective heaters 607, 608a, 608b. The deposition chamber 604 was equipped with a target 609 of Al of a purity of 99.99 % for depositing an Al layer on the sheet 602 by DC magnetron sputtering. The chambers 605a, 605b were equipped with targets 610a, 610b of ZnO of a purity of 99.9 % for depositing ZnO layers in succession by DC magnetron sputtering. There were provided four targets 610a while the target 610b was of a half width, in consideration of the deposition rate and the desired film thickness.

The rear reflective layer was formed with this apparatus in the following manner: The sheet was fed with a speed of 20 cm/min, and was heated to 250 °C at the ZnO deposition by the heater 608a only, while the heater 608b was not used. Argon was supplied with a pressure of 1.5 mTorr, and a DC voltage of 500 V was supplied to the cathodes, whereby obtained were currents of 6 A in the target 609, 4 A in each of the targets 610a and 2A in the target 610b. On the taken-up sheet the Al layer had a thickness of 1600 Å while the ZnO layer had an average thickness of 4300 Å in the total of two layer areas, and the ZnO layer had a turbid surface.

On thus obtained plate there was formed a tandem a-Si/a-SiGe photovoltaic device of the configuration shown in Fig. 11, in which there are shown a substrate 701; a metal layer 702; a transparent layer 703; a bottom cell 704; a top cell 708; a first layer area 703a of ZnO; a second layer area 703b of ZnO; n-type a-Si layers 705, 709; p-type $\mu\text{c-Si}$ layers 707, 711; an i-type a-SiGe layer 706; and an i-type a-Si layer 710. These semiconductor layers were prepared continuously in a roll-to-roll film forming apparatus as disclosed in the U.S. Patent No. 4,492,181. A transparent electrode 712 was deposited by a sputtering apparatus similar to the one shown in Fig. 8. A current-collecting electrode 713 was formed thereon. After the patterning of the transparent electrode and the formation of the current-collecting electrode, the sheet 602 was cut into pieces. The mass production was thus achieved, by effecting the entire process in continuous manner.

100 samples were prepared in this manner and evaluated under the irradiation of AM-1.5 (100 mW/cm²). There could be obtained an excellent photoelectric conversion efficiency of 11.5 ± 0.2 % in reproducible manner. Also after standing for 1000 hours under the conditions of a temperature of 50 °C and a relative humidity of 90 %, these devices showed a conversion efficiency of 11.0 ± 0.6 %, with almost no deterioration. Other 100 samples prepared in this manner, irradiated by the light corresponding to AM-1.5 for 600 hours in open state, showed an efficiency of 10.7 ± 0.3 %, indicating that the deterioration by light is also limited. These results were due to the tandem structure which enabled effective absorption to the longer wavelength region of the light thereby providing a higher output voltage, and also due to the reduced deterioration of the semiconductor layer under the light irradiation. Thus, in combination with the effect of the rear reflective layer of the present invention, there could be obtained a photovoltaic device of a high conversion efficiency and high reliability.

[Embodiment 8]

A rear reflective layer was formed in the same manner as in the embodiment 5, except for the use of a surface-polished Cu plate as the substrate. Then, on thus processed substrate and on a substrate without the deposition of ZnO layer of the second layer area, there were deposited Cu and In with respective thicknesses of 0.2 and 0.4 μ by sputtering. Subsequently the samples were transferred to a quartz glass bell jar, heated to 400 °C, and supplied with hydrogen selenide (H_2Se) diluted to 10 % with hydrogen to form a thin film of CuInSe_2 (CIS). Then a CdS layer of a thickness of 0.1 μ was formed thereon by sputtering, and annealing was conducted at 250 °C to form a p/b junction. Then a transparent electrode and a current-collecting electrode were formed thereon in the same manner as in the embodiment 5.

In the evaluation of thus obtained photovoltaic devices under the irradiation of AM-1.5 (100 mW/cm²), the devices with two ZnO layer areas showed a high conversion efficiency of 9.6 % while the devices with one ZnO layer area also showed a high efficiency of 9.5 %. However, in the measurement of I-V characteristics, the devices in which the shunt resistance per unit area does not exceed 200 Ω cm, were found in 4 % of all the devices with two layer areas and in 28 % of all the devices with one layer area. Consequently the reliability was higher in the two-layered structure.

[Embodiment 9]

10 In the present embodiment, there was prepared a PIN a-Si photovoltaic device of the configuration shown in Fig. 3, however without the metal layer 102. On a surface-polished Al plate 101 of a size of 5 x 5 cm and a thickness of 1 mm, there was deposited a ZnO layer 103c of a thickness of 1000 Å, in the apparatus shown in Fig. 6 employing a ZnO target, with the substrate at the room temperature. Then a ZnO layer 103d of an average thickness of 3000 Å was deposited thereon, with a substrate temperature of 300 °C, whereby the ZnO surface showed an irregular structure.

15 On thus obtained rear reflective layer, there were formed a PIN a-Si semiconductor layer 104, a transparent electrode 108 and a current-collecting electrode 109 in the same manner as in the embodiment 1 to complete a photovoltaic device. 10 samples were prepared in this manner and evaluated under the irradiation of AM-1.5 (100 mW/cm²). There was obtained an excellent photoelectric conversion efficiency of 9.6 ± 0.2 %, in reproducible manner. Also after standing for 1000 hours under the conditions of a temperature of 50 °C and a relative humidity of 90 %, these devices showed a conversion efficiency of 9.3 ± 0.5 %, with almost no deterioration.

[Embodiment 10]

25 In the present embodiment, there was prepared a PIN a-SiGe photovoltaic device of the configuration shown in Fig. 3. On a surface-polished stainless steel plate 101 of a size of 5 x 5 cm and a thickness of 1 mm, a Cu layer 102 of a thickness of 1500 Å, with a smooth surface, was formed by plating. Then Zn was ion plated in oxygen atmosphere with the substrate at the room temperature, thus depositing a ZnO layer of a thickness of 800 Å.

Subsequently a ZnO layer of a thickness of 1 μ , with an irregular surface structure, was deposited by effecting the ion plating again, with a substrate temperature of 250 °C.

10 samples were prepared by a subsequent process same as in the embodiment 9, except that the i-type layer was replaced by an a-SiGe layer which was deposited by introducing Si₂H₆ at 50 sccm, GeH₄ at 10 sccm and H₂ at 300 sccm, maintaining the internal pressure of the reaction chamber at 1 Torr, applying an electric power of 100 W and maintaining the plasma for 10 minutes. In the evaluation of these devices under the irradiation of AM-1.5 (100 mW/cm²), an excellent photoelectric conversion efficiency of 8.6 ± 0.4 % could be obtained in reproducible manner.

40 [Embodiment 11]

A rear reflective layer was formed in continuous manner with an apparatus shown in Fig. 9. In a feed chamber 603 there was set a roll 601 of an already washed stainless steel sheet of a width of 350 mm, a thickness of 0.2 mm and a length of 500 m. Said stainless steel sheet 602 was fed therefrom to a take-up chamber 606, through a metal layer deposition chamber 604, a first layer deposition chamber 605c and a second layer deposition chamber 605d. The sheet 602 could be heated to desired temperatures at respective deposition chambers, by means of heaters 607, 608c, 608d. The deposition chamber 604 was equipped with a target 609 of Al of a purity of 99.99 %, for depositing an Al layer on the sheet 602 by DC magnetron sputtering. The deposition chambers 605c, 605d were equipped with targets 610c, 610d of ZnO of a purity of 99.9 %, for depositing ZnO layers in succession by DC magnetron sputtering. The target 610c was of a half width, while there were provided four targets 610d, in consideration of the deposition rate and the desired film thicknesses.

This apparatus was employed in the formation of the rear reflective layer in the following manner. The sheet was fed with a speed of 20 cm/min, and was maintained at 250 °C at the ZnO deposition by the heater 608d only. The heater 608c was not employed, and the substrate was maintained at the room temperature. Argon was supplied with a pressure of 1.5 mTorr, and a DC voltage of 500 V was applied to the cathodes, whereby obtained were currents of 6 A in the target 609, 2 A in the target 610c, and 4 A in each of the targets 610d. On the taken-up sheet, the Al layer had a thickness of 1600 Å, while the ZnO

layer had an average thickness of 4400 Å in the total of two layer areas and had a turbid surface.

A tandem a-Si/a-SiGe photovoltaic device of the configuration shown in Fig. 12 was formed thereon. In Fig. 12 there are shown a substrate 701; a metal layer 702; a transparent layer 703; a bottom cell 704; a top cell 708; a first layer area 703c; a second layer area 703d; n-type a-Si layers 705, 709; p-type μ c-Si layers 707, 711; an i-type a-SiGe layer 706; and an i-type a-Si layer 710. These semiconductor layers were prepared in continuous manner, with a roll-to-roll film forming apparatus as disclosed in the U.S. Patent No. 4,492,181. A transparent electrode 712 was deposited in a sputtering apparatus similar to the one shown in Fig. 9. A current-collecting electrode 713 was formed thereon. After the patterning of the transparent electrode and the formation of the current-collecting electrode, the sheet 602 was cut into pieces. The mass production could be achieved, by effecting the entire process in continuous manner.

100 samples were prepared in this manner and evaluated under the irradiation of AM-1.5 (100 mW/cm²). There could be obtained an excellent photoelectric conversion efficiency of 11.3 ± 0.2 % in reproducible manner. Also after standing for 1000 hours under the conditions of a temperature of 50 °C and a relative humidity of 90 %, these devices showed a conversion efficiency of 11.1 ± 0.6 %, with almost no deterioration. Also other 100 samples prepared in this method showed, after irradiation with the light corresponding to AM-1.5 for 600 hours in open state, a conversion efficiency of 10.7 ± 0.3 %, indicating that the deterioration by light is also limited. These results were due to the tandem structure which enabled efficient absorption to the longer wavelength region of the light, thereby elevating the output voltage, and also due to the reduced deterioration of the thin film semiconductor layer under the light irradiation. Thus, in combination with the effect of the rear reflective layer of the present invention, there could be obtained a photovoltaic device of a high conversion efficiency and high reliability.

[Embodiment 12]

A rear reflective layer was prepared in the same manner as in the embodiment 9, except for the use of a surface-polished Cu plate as the substrate. Then, on thus treated substrate and on a substrate lacking the deposition of the second ZnO layer area, Cu and In were deposited with respective thicknesses of 0.2 and 0.4 μ by sputtering. Subsequently the samples were transferred to a quartz glass bell jar, heated to 400 °C and supplied with hydrogen selenide (H₂Se) diluted to 10 % with hydrogen, for forming a thin film of CuInSe₂ (CIS). Then a CdS layer was deposited thereon with a thickness of 0.1 μ by sputtering, and annealing was conducted at 250 °C to form a p/n junction. A transparent electrode and a current-collecting electrode were formed thereon in the same manner as in the embodiment 9.

In the evaluation of these photovoltaic devices under the irradiation of AM-1.5 (100 mW/cm²), the device with two ZnO layer areas showed an excellent conversion efficiency of 9.6 % while the device with a smooth ZnO layer only showed an inferior conversion efficiency of 8.3 %. These results indicate that the present invention is effective also to semiconductors other than a-Si.

[Embodiment 13]

This embodiment shows that the handling of a secondary battery, such as nickel-cadmium (NiCd) battery, can be extremely facilitated by integrating said battery with a solar cell, constituting an example of the photovoltaic device produced by the method of the present invention.

A tandem a-Si/a-SiGe photovoltaic device was prepared in the same manner as in the embodiment 3, except that the roll of the stainless steel sheet substrate was replaced by a roll of a sheet of cold-rolled steep plate of JISG3141 with a width of 350 mm and a thickness of 0.015 mm, provided with nickel plating of a thickness of 5 μ . The transparent electrode was patterned in a size of 58 x 100 mm, and, after the formation of the current-collecting electrode, the device was cut into a size of 70 x 110 mm. Fig. 13 shows a battery employing thus prepared photovoltaic device as the container. Fig. 13A is an external view of said battery.

On the container 1501, there is incorporated the photovoltaic device as explained above, and a sturdy bottom plate is provided for withstanding the pressure of the gas generated inside. Said bottom plate does not have the photovoltaic device and serves as the cathode terminal. Fig. 13B shows the internal structure of the battery. Inside the battery there are wound a cathode plate 1504 and an anode plate 1505, separated by a separator 1506. Said plates 1504, 1505 are composed of sintered Ni-Cd alloy, while the separator 1506 is composed of nylon non-woven cloth impregnated with electrolyte solution of potassium hydroxide. The cathode plate 1504 is connected to the container 1501, while the anode plate 1505 is connected to an anode terminal 1502. The interior is sealed with a plastic lid 1507, equipped with a packing 1508, for avoiding the electrolyte leakage. However, the lid 1507 is provided with a safety valve 1509, in order to

prevent accident resulting from a rapid pressure increase at rapid charging or discharging.

A grid electrode 1513 on the surface of the photovoltaic device is connected to a lead wire, which is connected to the anode terminal 1502 through a diode 1503 for preventing inverse current. In order to protect the surface of the photovoltaic device, a cylindrical heat-shrinkable sheet is placed on the container and heated with hot air, thereby covering the battery except the anode terminal 1505 and the bottom plate. Fig. 14 shows an equivalent circuit of the above-explained connections. The battery 1510 is connected, by the cathode terminal (bottom plate) 1501 and the anode terminal 1502, to an external load 1512.

When the photovoltaic device 1511 is irradiated with light, there is generated a photovoltaic force of about 1.6 V, which is applied to the battery 1510. As the voltage of the battery is about 1.2 V at maximum, so that the diode 1503 is biased in the forward direction, and the battery 1510 is charged by the photovoltaic device 1511.

However, when the photovoltaic device 1511 is not irradiated with light, the diode 1503 is biased in the inverse direction, so that the current is not supplied unnecessarily from the battery 1510. Also in case the battery is charged in an ordinary charger, the charging can be achieved in usual manner, without the waste of current in the photovoltaic device 1511, by the function of said diode 1503. Consequently the battery of the present embodiment, equipped with the photovoltaic device, can be charged by light, by being taken out from the battery case after use and being left in a place with strong light irradiation such as window side, or even within the battery case if it has a transparent cover. This battery is particularly convenient for use outdoors, since it does not require a particular charger. It can also be charged with an ordinary charger, in case a rapid charging is required. It can also be formed in the same manner as the ordinary batteries, such as UM1, UM2 or tank-shaped battery. It can therefore be used in various electric appliances and has smart appearance.

Two such batteries are loaded in a portable electric torch, and, when they are exhausted, are taken out and let to stand at a sunny window side for charging. After a fine day, they are sufficiently charged and can be used again in the electric torch.

[Embodiment 14]

In the artificial satellite, there is generally employed a compound crystalline solar cell, such as of InP, which has a large output per unit area and is resistant to radiation. However, since such solar cell is composed of wafers, it has to be fixed on a panel. At the satellite launching, the panel has to be compactized and requires a complex fold-unfold mechanism for a plurality of panels. For this reason, even if the output per unit area is high, the output per unit weight has had to be considerably low.

The present embodiment provides a large output per unit weight with a simple mechanism in the satellite power source, through the use of a solar cell, as an example of the photovoltaic device produced by the method of the present invention.

A tandem a-Si/a-SiGe photovoltaic device was prepared in the same manner as in the embodiment 13, except that the roll of stainless steel substrate was replaced by a roll of an aluminum plate of JIS2219 (including copper, manganese etc.) of a width of 350 mm and a thickness of 0.15 mm. A transparent electrode 1512 was patterned into a size of 105 x 320 mm, and, after the formation of a current-collecting electrode 1513, the sheet was cut into pieces. An end of the longer side of each photovoltaic device was polished with a grinder to expose the substrate surface. Then the devices were serially connected as shown in Fig. 15. The devices 1701 and 1702 were connected, with a mutual distance of about 5 mm, from the rear side by means of an insulating film 1703 composed for example of polystyrene, polyimide, cellulose triacetate or trifluoroethylene, and the current-collecting electrode 1513 of the device 1701 and the exposed substrate portion 1704 of the device 1702 were connected by heat pressing with a copper sheet 1705 utilizing copper ink or silver ink. For avoiding the shortcircuiting between the copper sheet 1705 and the substrate of the device 1701, a polyimide film 1706 is applied on the edge portion. A protective polyester film 1707 was adhered thereon.

200 photovoltaic devices were serially connected to form a solar cell of a length of about 20 m, as an application of the photovoltaic device. Said solar cell can be constructed as shown in Fig. 16. The main body 1901 of the satellite is provided with a rotatable shaft 1902, on which sheet-shaped photovoltaic devices 1903, 1904 etc. are wound. 1903 indicates a completely extended state of the device while 1904 indicates a half wound state. The current generated at the end of the sheet-shaped photovoltaic device is supplied to the main body of the satellite, by means of an unrepresented cable that can be wound together with the photovoltaic device. Said sheet-shaped photovoltaic devices 1903, 1904 and said cable can be extended or wound by an unrepresented driving system.

This system is used in the following manner. At the launching of the satellite, the sheet-shaped photovoltaic devices 1903, 1904 are maintained in the wound state. After the satellite is placed on the orbit, it is made to rotate slowly about the rotary axis directed toward the sun. At the same time the sheet-shaped photovoltaic devices are slowly extended, whereby they are stretched radially by centrifugal force and start power generation. In case of the orbit change, position change Or recovery of the satellite, the sheet-shaped photovoltaic devices are wound for example by a motor. Thereafter they can be extended again, when required, to re-start the power generation. A system with six sheets of the photovoltaic devices has a maximum output of 5 kW with a total weight of ca. 30 kg including the driving system, so that a large output per unit weight can be achieved.

[Embodiment 15]

The present embodiment provides a roofing material obtained by ondular forming of the photovoltaic devices produced by the method of the present invention. A photovoltaic device prepared according to the method of the embodiment 3 was cut into a length of 100 mm and a width of 900 mm, then the obtained sheets were individually pressed into ondular form and adhered corrugated boards of a length of 1800 mm and a width of 900 mm, composed for example of polyvinyl chloride resin or polyester resin. Fig. 17 shows the details of connection of the photovoltaic devices. Devices 2001 and 2002 are adhered, with a mutual distance of 10 mm, on a corrugated board 2003.

A grid electrode of the device 2001 and an exposed substrate portion of the device 2002 are connected by a copper sheet 2005. There is provided an insulating film 2006 for preventing the shortcircuiting, composed for example of polyimide resin, polyvinyl alcohol resin or polystyrene resin. Nail holes 2007 are provided in advance in the corrugated board 2003, for fixing the roofing material. For avoiding the shortcircuiting, the copper sheet 2005 is provided with holes 2008 larger than said nail holes. However said nail holes are provided only in the necessary serial connecting part. A PVA resin layer 2009 and a fluorinated resin layer 2010 were superposed thereon and adhered by pressurized heating to obtain an integral roofing material. Fig. 18 shows a roof obtained with said roofing materials (number of ondulations in each integral roofing material 2102 being reduced for the purpose of simplicity). Fig. 17 shows the details of each photovoltaic device 2101 of the roofing material 2102. At the serial connecting portions 2103, 2104, it is connected to the neighboring photovoltaic devices. The serial connecting portion 2103 has nail holes but that 2104 does not have nail holes. It is fixed, with overlapping of an ondulation with another roofing material 2105. The photovoltaic device is not present at the left-hand end of the roofing material 2102. Since the corrugated board is transparent, it does not hinder the light even if it is placed on the adjacent roofing material 2105. The output terminal at the left-hand end of the roofing material 2102 is connected in advance with the output terminal at the right-hand end of the material 2105 before the material 2102 is placed on the portion 2106, and the connecting part is sealed for example anticorrosive paint and is so positioned as not to be exposed to the exterior. In this manner the serial connection is completed simultaneously with the installation of plural roofing materials.

If the serial connection is not conducted, the output terminal of each device can be connected to a cable which can be guided under a heaved portion 2108 for supplying the output to the exterior.

A serial connection of four of such roofing materials, when connected in parallel in 8 sets and installed on a roof inclined by 30° toward the south, provides an output of about 5 kW in the summer daytime, enough as the electric power source for an ordinary household.

[Embodiment 16]

The present embodiment provides a photovoltaic device for automobile, usable for driving a ventilation fan or preventing the discharge of battery. The photovoltaic devices are starting to be employed in the automobiles, but they are generally installed on the sun roof or on the stabilizer fin, in order not to affect the automobile design. In fact a suitable place for installation is difficult to find in automobiles of ordinary specifications. The engine room cover or the ceiling is adequate for receiving the sunlight, but the installation in these locations may easily affect the design of the automobile. Also the front, rear or lateral face of the automobile is susceptible to damages by contact. On the other hand, the rear quarter pillars of the automobile can provide a suitable area, are relatively free from damages and allow easy matching with the automobile design.

The present embodiment utilizes the feature of the photovoltaic device of the present invention, constructed on a sheet-shaped metal substrate, and provides a photovoltaic device having a curved form that can be integrated with the automobile body when installed on the rear quarter pillars.

A photovoltaic device was prepared in the same manner as in the embodiment 14, and individual photovoltaic pieces were obtained by effecting the patterning of the transparent electrode, the formation of the current-collecting electrode and the cutting according to the automobile design.

Thus obtained pieces were serially connected according to the method of the embodiment 15. For use in an automobile equipped with a battery of 12 V, Fig. 19 shows a configuration consisting of 10 solar cell pieces. Pieces 2201 in the upper portion of the pillar are made longer because of the smaller width, while those 2202 in the lower portion are made shorter because of the larger width, in such a manner that all the pieces have substantially same areas. Also the current-collecting electrodes 2203 are provided denser for the longer pieces, in order to suppress the power loss resulting from the resistance in the transparent electrode.

The color of the photovoltaic devices is an important factor in the design, but the thickness of the transparent electrode can be regulated so as to match the color of other parts of the automobile. An ITO transparent electrode with an ordinary thickness of 650 Å provides purple appearance. Said color becomes yellow-green at a thickness range of 450 - 500 Å, brownish in 500 - 600 Å, purple in 600 - 700 Å, and more bluish in 700 - 800 Å. The output of the photovoltaic device is somewhat lowered when the thickness of the ITO layer is deviated from the standard value, but the loss in efficiency can be minimized in case of a tandem cell, by adjusting the spectral sensitivities of the top and bottom cells, by forming the top cell thinner for a thinner ITO layer because the spectral sensitivity is shifted toward the shorter wavelength, and forming the top cell thicker for a thicker ITO layer.

The photovoltaic modules 2302 of the present embodiment were installed on the left and right rear quarter pillars of a 4-door sedan automobile 2301 (coated blue) shown in Fig. 20. Fig. 19 shows the module for use on the left-side pillar. Said devices are incorporated in a circuit shown in Fig. 21, in which the left device 2401 and the right device 2402 are connected to a battery 2405 respectively through diodes 2403, 2404. A ventilation fan is activated when the indoor temperature is high because of the strong sunlight. A switch 2407 for the ventilation fan 2406 is turned on only when at least either of current sensors 2409, 2410 for detecting the output currents from the left and right photovoltaic devices provides a high-level signal and a temperature sensor 2408 provides a high-level signal.

Such photovoltaic modules allowed to reduce the indoor temperature, which easily reached 80 °C in a fine summer day, by about 30 °C, and also avoided the exhaustion of the battery even when it is left unused for a week in the mid winter season. Such configuration is also usable in the snowy district, because the snow accumulated on the rear quarter pillars quickly melted by sunlight.

Table 1

Sample	Substrate	Metal layer	Transparent layer	Conversion efficiency
1a	stainless steel plate (SUS 430)	Al (1500Å) smooth surface	ZnO (4000Å) irregular structure	9.8%
1b	stainless steel plate	Al, irregular	ZnO	8.0%
1c	stainless steel plate	Al, smooth	ZnO, smooth	8.2%
1d	stainless steel plate	-	-	6.7%
1e	aluminum plate	-	ZnO, irregular	9.6%

Table 2

Sample	Substrate	Metal layer	Transparent layer	Conversion efficiency
2a	stainless steel plate (SUS 430)	silver, smooth	ZnO, irregular	10.0%
2b	stainless steel plate	silver, irregular	ZnO, irregular	2.7%

Table 3

Sample	Substrate	Metal layer	Transparent layer	Conversion efficiency
3a	stainless steel plate (SUS 430)	Al (1500Å) smooth	ZnO (non-doped), irregular	1.5%
3b	stainless steel plate	Al, smooth	ZnO (Cu doped) irregular	7.4%

Table 4

Sample	Substrate	Metal layer	Transparent layer		Conversion efficiency
			1st layer area	2nd layer area	
6a	stainless steel plate (SUS 430)	Al (1500Å), irregularity 1000Å	ZnO (4000Å) pitch 4000-9000Å height 2000-4000Å	ZnO (500Å)	10.0%
6b	ibid.	Al (1500Å), irregularity 20000Å	ibid.	ibid.	8.5%
6c	ibid.	Al (1500Å), irregularity 1000Å	ibid.	-	9.7%
6d	ibid.	ibid.	ZnO (4500Å) pitch 4000-9000Å height 2000-4000Å	-	9.6%
6e	ibid.	ibid.	ZnN (4000Å) pitch 2500Å max. height 500Å max.	-	8.2%
6f	ibid.	ibid.	ZnO (4500Å) pitch 2500Å max. height 500Å max.	-	8.0%
6g	aluminum	-	ZnO (4000Å) pitch 4000-9000Å height 2000-4000Å	ZnO (500Å)	9.8%

Table 5

Sample	Substrate	Metal layer	Transparent layer		Conversion efficiency
			1st layer area	2nd layer area	
7a	stainless steel (SUS 430)	Al (1500Å), irregularity 1000Å	ZnO (10000Å) pitch 6000-10000Å height 3000-8000Å	ZnO (500Å)	9.9%
7b	ibid.	ibid.	ZnO (25000Å) pitch 6000-10000Å height 3000-8000Å	ibid.	9.7%
7c	ibid.	ibid.	ZnO (25000Å) pitch 9000-14000Å height 5000-10000Å	ibid.	9.4%
7d	ibid.	ibid.	ZnO (25000Å) pitch 18000-28000Å height 8000-15000Å	ibid.	8.6%

Table 6

Sample	Substrate	Metal layer	Transparent layer		Conversion efficiency
			1st layer area	2nd layer area	
9a	stainless steel plate (SUS 430)	Al (1500Å) irregularity pitch 1000Å	ZnO (1000Å) irregularity pitch 1000Å	ZnO (3000Å) pitch 4000-8000Å height 2000-3000Å	9.9%
9b	ibid.	Al (1500Å) irregularity pitch 2000Å	ZnO (1000Å) irregularity pitch 1500Å	ZnO (3000Å)	8.7%
9c	ibid.	Al (1500Å) irregularity pitch 1000Å	ZnO (1000Å) irregularity pitch 1000Å	-	8.3%
9d	ibid.	ibid.	ZnO (4000Å) pitch 2500Å max. height 500Å max.	-	8.2%
9e	ibid.	ibid.	ZnO (4000Å) pitch 4000-9000Å height 2000-4000Å	-	9.7%
9f	aluminum plate	-	ZnO (1000Å) irregularity pitch 1000Å	ZnO (3000Å) pitch 4000-8000Å height 2000-3000Å	9.7%

Table 7

Sample	Substrate	Metal layer	Transparent layer	Conversion efficiency
10a	stainless steel plate (SUS 430)	silver, smooth	two-layered, with irregular structure in the 2nd ZnO layer area	10.3%
10b	stainless steel plate	silver, irregular	two-layered ZnO, irregular structure	2.9%

Table 8

Sample	Substrate	Metal layer	Transparent layer		Conversion efficiency
			1st layer area	2nd layer area	
11a	stainless steel plate (SUS 430)	Al (1500Å) irregularity pitch 1000Å	SnO ₂ (1500Å) irregularity pitch 1000Å	ZnO (10000Å) pitch 6000-9000Å height 4000-7000Å	9.5%
11b	ibid.	ibid.	ibid.	ZnO (10000Å) pitch 8000-15000Å height 8000-10000Å	9.2%
11c	ibid.	ibid.	ibid.	ZnO (25000Å) pitch 6000-9000Å height 4000-7000Å	9.3%
11d	ibid.	ibid.	ibid.	ZnO (25000Å) pitch 8000-15000Å height 8000-13000Å	9.1%
11e	ibid.	ibid.	ibid.	ZnO (25000Å) pitch 17000-26000Å height 10000-16000Å	8.5%

Table 9

Sample	Subst. temp.	Appearance	SEM observation
13a	room temp.	lustrous	irregularity of a pitch of ca. 1000Å
13b	100 °C	slightly turbid	irregularity of a pitch of ca. 2000Å
13c	200 °C	turbid	irregularity of a pitch 4000 - 7000Å
13d	300 °C	turbid	irregularity of a pitch 4000 - 10000Å

Table 10

Sample	subst. temp.	Appearance	SEM observation
14a	room temp.	slightly yellowish lustrous	irregularity of a pitch of ca. 1000Å
14b	100 °C	transparent, lustrous	irregularity of a pitch of ca. 1500Å
14c	200 °C	turbid	irregularity of a pitch 3000 - 7000Å
14d	300 °C	turbid	irregularity of a pitch 4000 - 9000Å

Table 11

Sample	Subst. temp.	Appearance	SEM observation
I5a	room temp.	slightly yellowish lustrous	irregularity of a pitch of ca. 1000 Å
I5b	100 °C	transparent, lustrous	irregularity of a pitch of ca. 1500 Å
I5c	200 °C	turbid	irregularity of a pitch of 3000 - 7000 Å and a height 1500 - 3000 Å
I5d	300 °C	turbid	irregularity of a pitch of 4000 - 9000 Å and a height of 1500 - 4000 Å
I5e	200 °C, immersed in 10% acetic acid soln. for 1 min.	turbid	pitch 6000 - 10000 Å height 3000 - 8000 Å
I5f	200 °C, immersed in 10% acetic acid soln. for 1.5 min.	turbid	pitch 9000 - 14000 Å height 5000 - 10000 Å

Table 12

Sample	Subst. temp.	Appearance	SEM observation
I6a	room temp.	slightly yellowish, lustrous	irregularity of a pitch of ca. 1000 Å
I6b	100 °C	transparent, lustrous	irregularity of a pitch of ca. 1500 Å
I6c	200 °C	turbid	irregularity of a pitch of 3000 - 7000 Å and a height of 1500 - 3000 Å
I6d	300 °C	turbid	irregularity of a pitch of 4000 - 9000 Å and a height of 2000 - 4000 Å

The rear reflective layer of the present invention elevates the light reflectance and achieves effective trapping of light in the semiconductor, whereby the light absorption there is increased and a photovoltaic device of a high conversion efficiency can be obtained. Also the reliability of the photovoltaic device is improved since the diffusion of metal atoms into the semiconductor film is suppressed, also since the leak current is suppressed by a suitable electrical resistance even in the presence of local shortcircuitings in the semiconductor, and since a higher chemical resistance reduces the danger of new defect formation in the subsequent process.

Also even if the metal layer becomes exposed in the formation of the irregular surface structure which is required for realizing the effective optical trapping effect, the diffusion of metal atoms from thus exposed area to the semiconductor layer can be prevented by the formation of a second layer area. Furthermore, the frequency of leak current between thus exposed area and the upper electrode through local shortcircuitings in the semiconductor can be extremely reduced by the formation of said second layer area, whereby the reliability of the photovoltaic device can be improved.

Furthermore, such rear reflective layer can be produced as a part of the mass production method, such as a roll-to-roll method. As explained above, the present invention contributes greatly to the practical applications of the photovoltaic devices.

A photovoltaic device comprises a metal with a smooth surface; a transparent layer formed on the smooth surface; and a photoelectric conversion layer formed on the transparent layer. The transparent layer has an irregular surface at a side opposite to the smooth surface.

Claims

1. A photovoltaic device comprising a metal with a smooth surface; a transparent layer formed on said smooth surface; and a photoelectric conversion layer formed on said transparent layer, wherein said transparent layer has an irregular surface at a side opposite to said smooth surface.
2. A photovoltaic device according to claim 1, wherein said transparent layer includes plural layer areas.
3. A photovoltaic device according to claim 1, wherein said transparent layer contains an impurity for elevating the electrical resistance thereof.

4. A photovoltaic device according to claim 1, wherein said transparent layer is composed of ZnO and said impurity is Cu.
5. A photovoltaic device according to claim 1, wherein said transparent layer is composed of SnO₂ and said impurity is Al.
6. A photovoltaic device according to claim 2, wherein, in said plural layer areas of the transparent layer, a layer area at the side of said metal layer has a higher specific resistivity than in a layer area at the side of the photoelectric conversion layer.
7. A photovoltaic device according to claim 2, wherein a layer area at the side of said metal layer is thicker than a layer area at the side of said photoelectric conversion layer.
8. A photovoltaic device according to claim 2, wherein a first layer area of the transparent layer, in contact with said smooth surface, has an irregular surface opposite to said smooth surface.
9. A photovoltaic device according to claim 8, wherein said smooth surface has a pitch of irregularity not exceeding 1000 Å and the irregular surface of said first layer area has a pitch of irregularity within a range from 3000 to 20000 Å and a magnitude of irregularity of 500 Å.
10. A photovoltaic device according to claim 2, wherein said transparent layer includes plural layer areas, also at least a layer area provided in contact with the smooth surface of said metal has a smooth surface at the side of said photoelectric conversion layer, and at least a layer area, other than the layer area(s) mentioned above, has an irregular surface at the side of said photoelectric conversion layer.
11. A photovoltaic device according to claim 10, wherein said smooth surface has a pitch of irregularity not exceeding 1000 Å while the smooth surface, at the side of said photoelectric conversion layer, of at least a layer area in contact with said metal has a pitch of irregularity not exceeding 3000 Å, and the irregular surface of said at least an irregular layer area has a pitch of irregularity within a range from 3000 to 20000 Å and a magnitude of irregularity within a range from 500 to 20000 Å.
12. A photovoltaic device according to claim 1, wherein a surface of said photoelectric conversion layer, positioned opposite to the transparent layer, has irregularity comparable to that of said transparent layer.
13. A method for producing a photovoltaic device provided with a metal with a smooth surface, a transparent layer, and a photovoltaic layer, which comprises utilizing the difference in forming temperatures in forming plural layer areas in said transparent layer and forming an irregular surface structure in a layer area in contact with the smooth surface of said metal, and satisfying a relation $T_1 > T_n$ between a first layer forming temperature T_1 and at least a layer forming temperature T_n among the forming temperatures for the second and subsequent layer areas, wherein said layer forming temperatures are numbered as the first layer forming temperature T_1 , the second layer forming temperature T_2 etc. from the metal side.
14. A method for producing a photovoltaic device provided with a metal having a smooth surface, a transparent layer, and a photovoltaic layer, which comprises utilizing the difference in forming temperatures in forming plural layer areas in said transparent layer and forming an irregular surface structure in at least a layer area other than the one in contact with the smooth surface of said metal, and satisfying a relation $T_1 < T_n$ between a first layer forming temperature T_1 and a layer forming temperature T_n among the forming temperatures for the second and subsequent layer areas, wherein said layer forming temperatures are numbered as the first layer forming temperature T_1 , the second layer forming temperature T_2 etc. from the metal side.
15. A method for producing a photovoltaic device according to claim 13, wherein the irregular surface structure is formed in said transparent layer, by depositing a layer area in which said irregularity is to be formed and then immersing the surface of said layer area in aqueous solution of an acid, an alkali or a salt.

16. A method according to claim 15, wherein said acid is acetic acid, sulfuric acid, hydrochloric acid, nitric acid or perchloric acid, said alkali is sodium hydroxide, potassium hydroxide or aluminum hydroxide, and said salt is ferric chloride or aluminum chloride.

17. A battery comprising a photovoltaic device on a battery container, wherein at least an electrode of the photoelectric conversion layer of said device is connected to a diode for blocking inverse current.

18. An artificial satellite, comprising a photovoltaic device of the claim 1 provided on a windable substrate, a rotary shaft for winding said photovoltaic device, and a power source for driving said rotary shaft.

19. A roofing material comprising a corrugated board, at least a photovoltaic device of the claim 1 formed on said corrugated board, a conductive sheet and a resinous material, wherein connections at least between said photovoltaic devices are made by said conductive sheet, and a surface of said devices opposite to said corrugated board is covered with said resinous material.

20. A photovoltaic module comprising a plurality of the photovoltaic devices of the claim 1, and current-collecting electrodes, wherein serially connected devices have mutually equal light-receiving areas, and the density of said current-collecting electrodes is made higher in case said photovoltaic devices are connected long in series.

21. A photovoltaic module according to claim 20, wherein the thickness of the transparent electrode constituting said photovoltaic devices is varied.

22. An automobile equipped with the photovoltaic modules according to claim 21, on the rear quarter pillars.

23. A method for producing a photovoltaic device according to claim 14, wherein the irregular surface structure is formed in said transparent layer, by depositing a layer area in which said irregularity is to be formed and then immersing the surface of said layer area in aqueous solution of an acid, an alkali or a salt.

FIG. 1

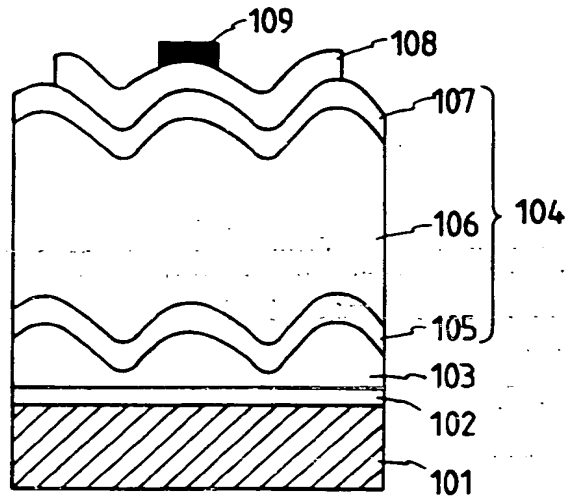


FIG. 2

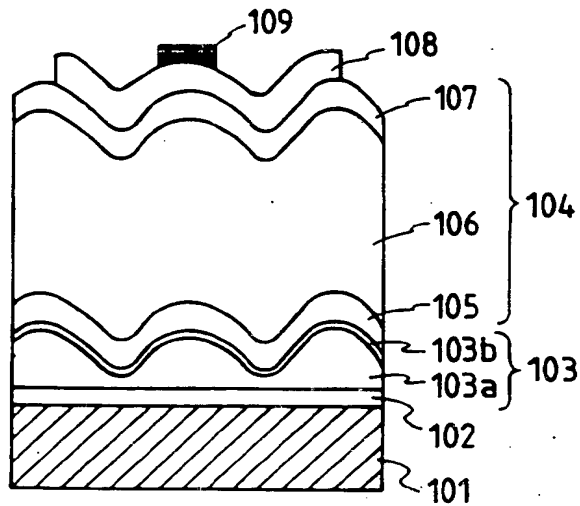


FIG. 3

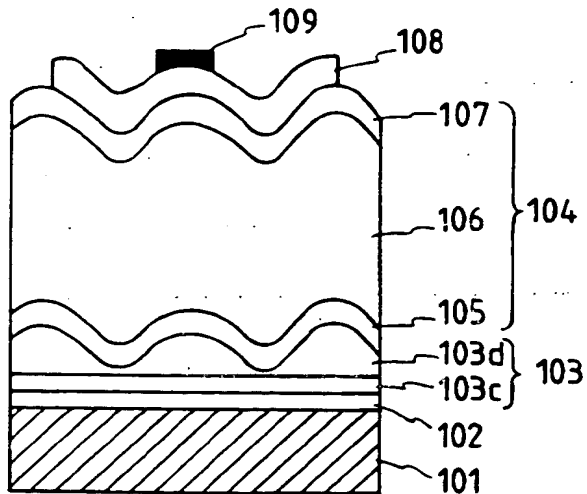


FIG. 4A

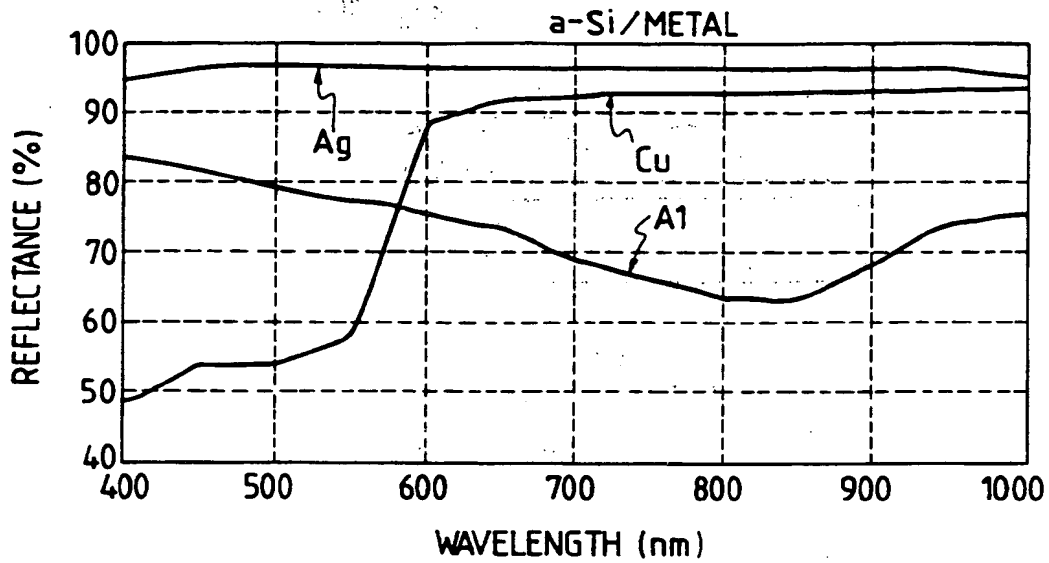


FIG. 4B

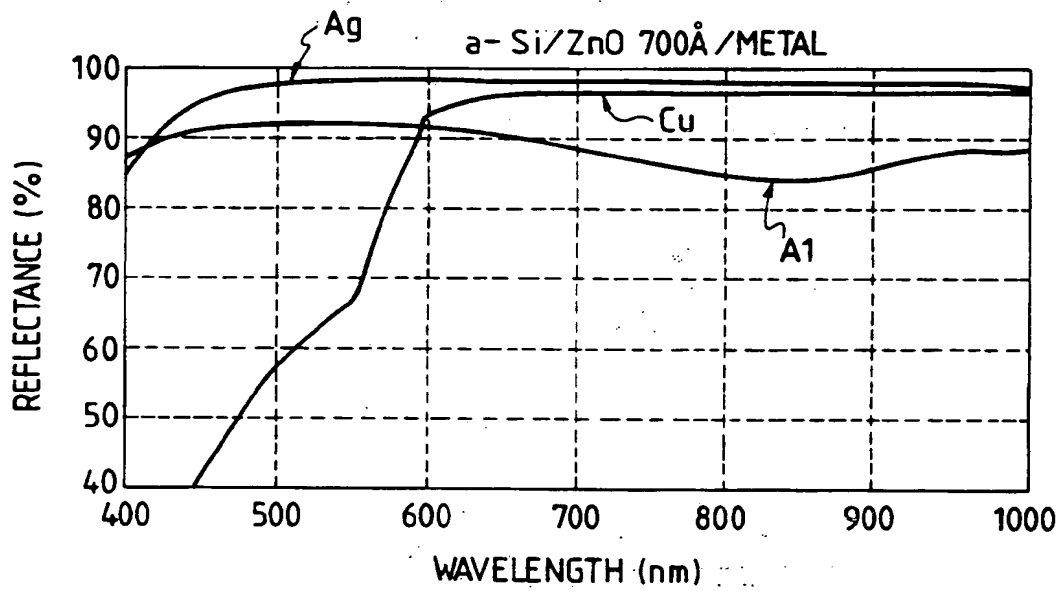


FIG. 5

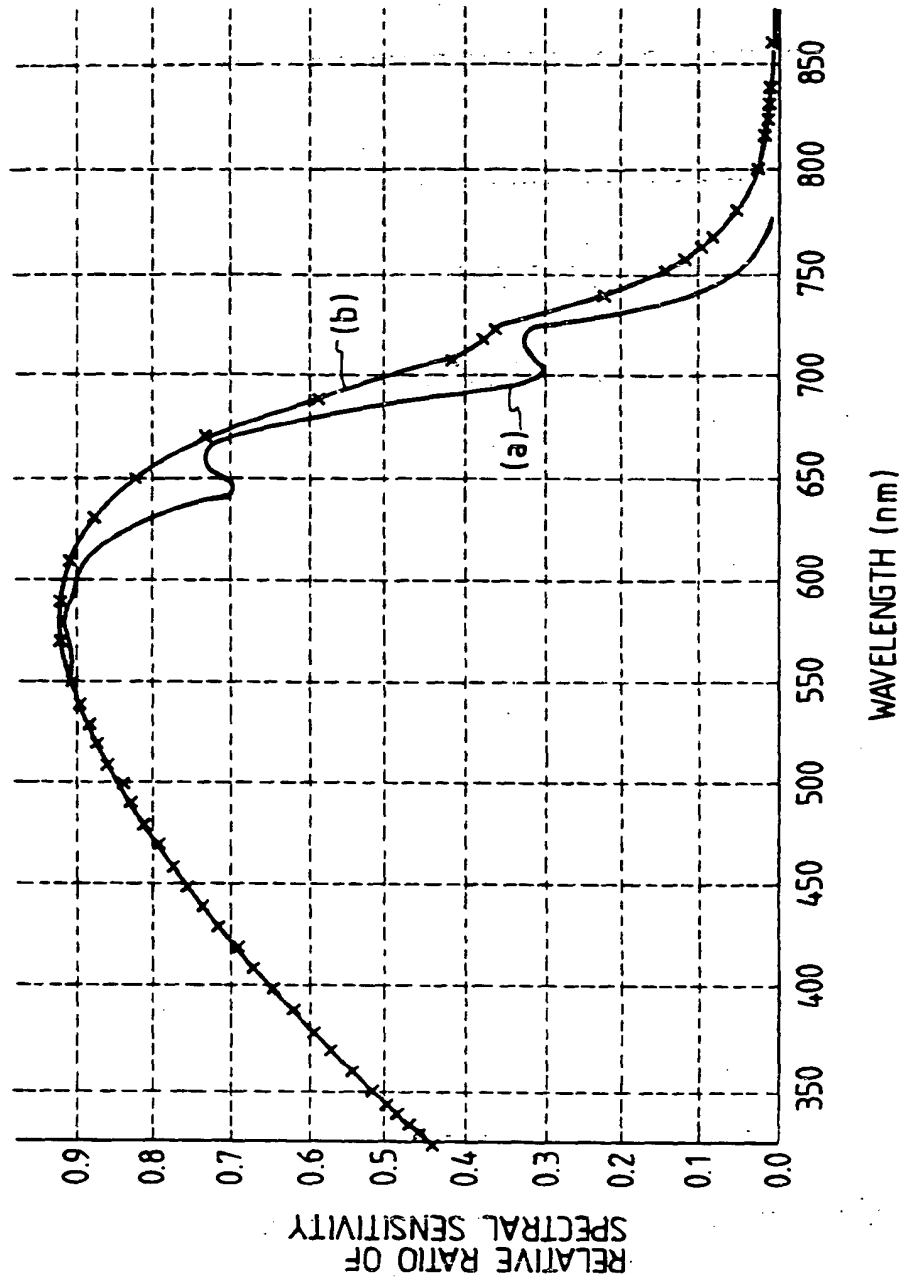


FIG. 6

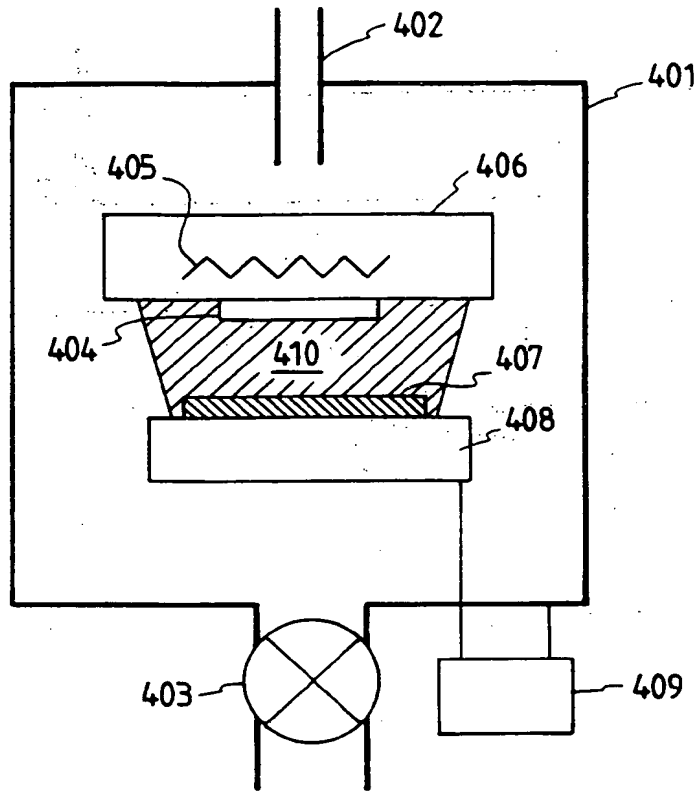


FIG. 7

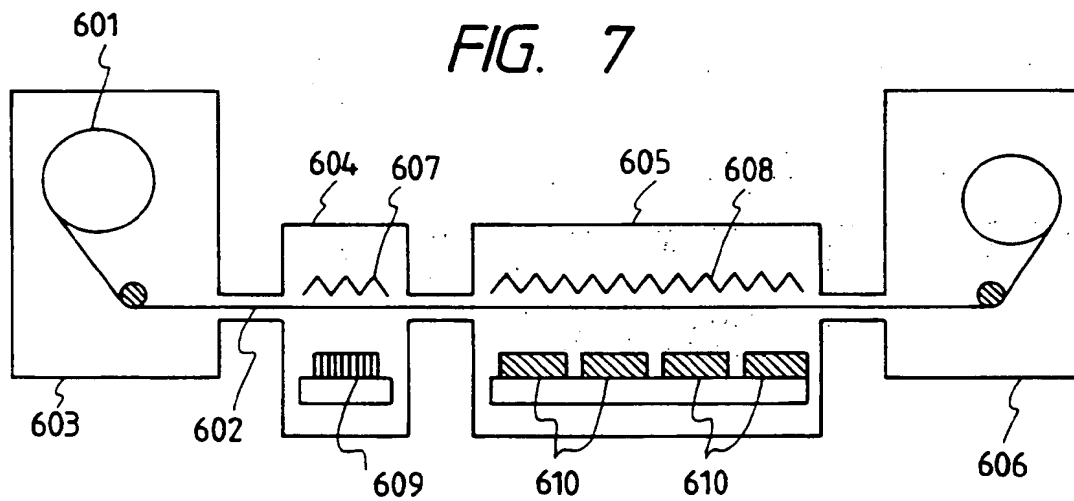


FIG. 8

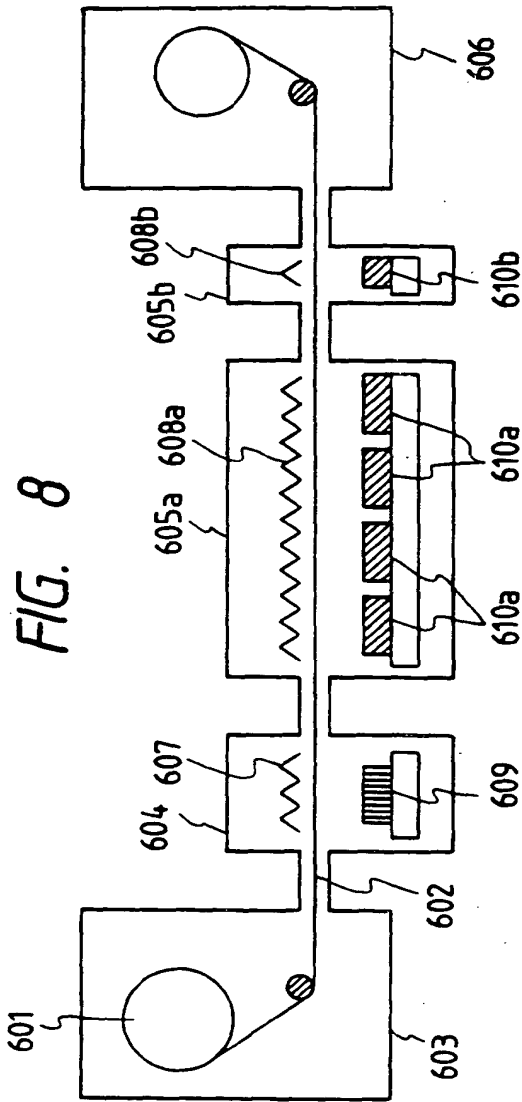


FIG. 9

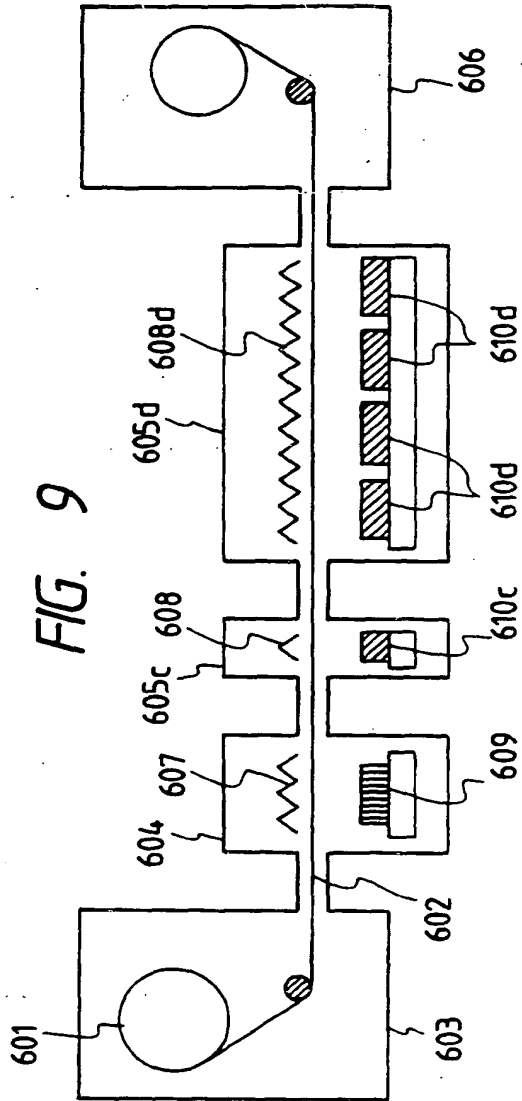


FIG. 10

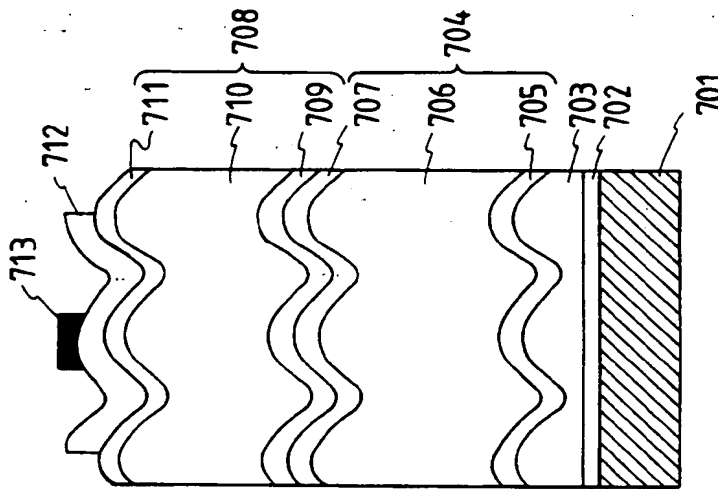


FIG. 11

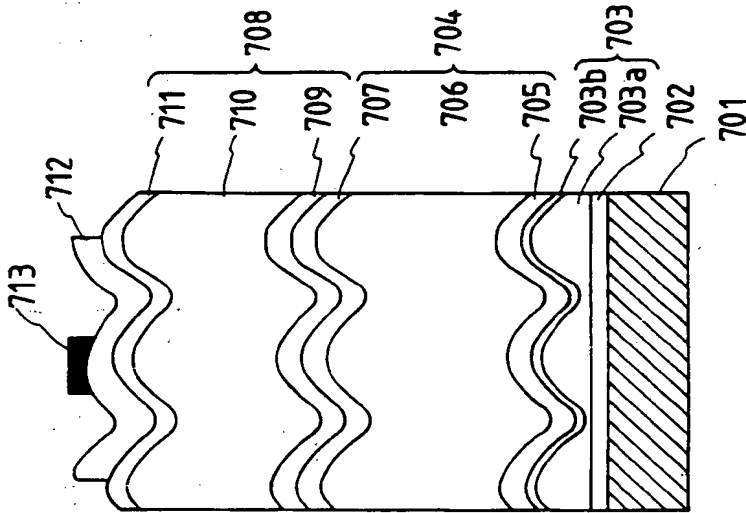


FIG. 12

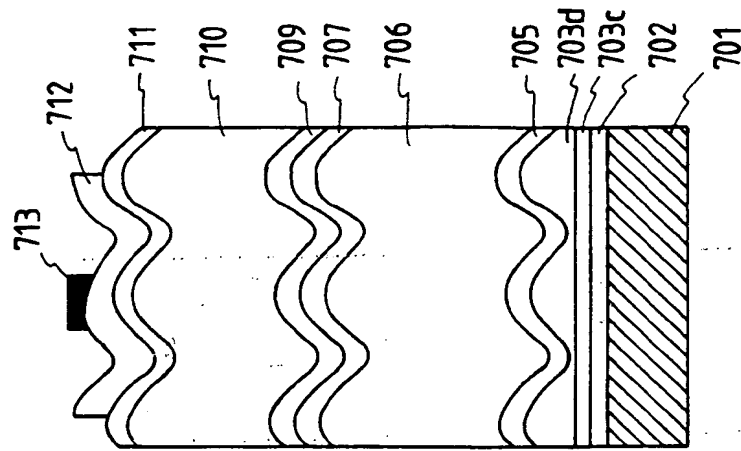


FIG. 13A

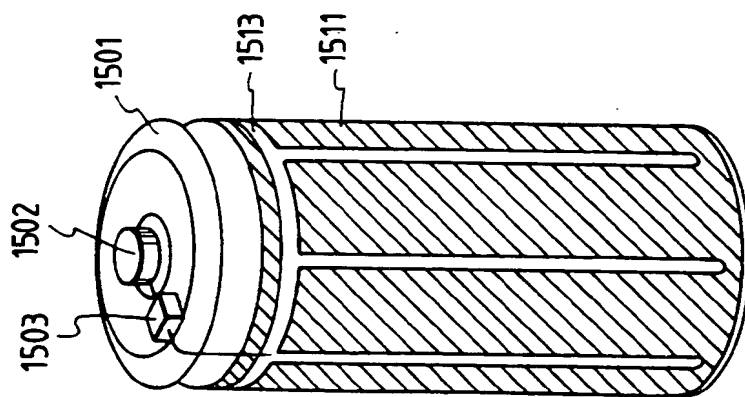


FIG. 13B

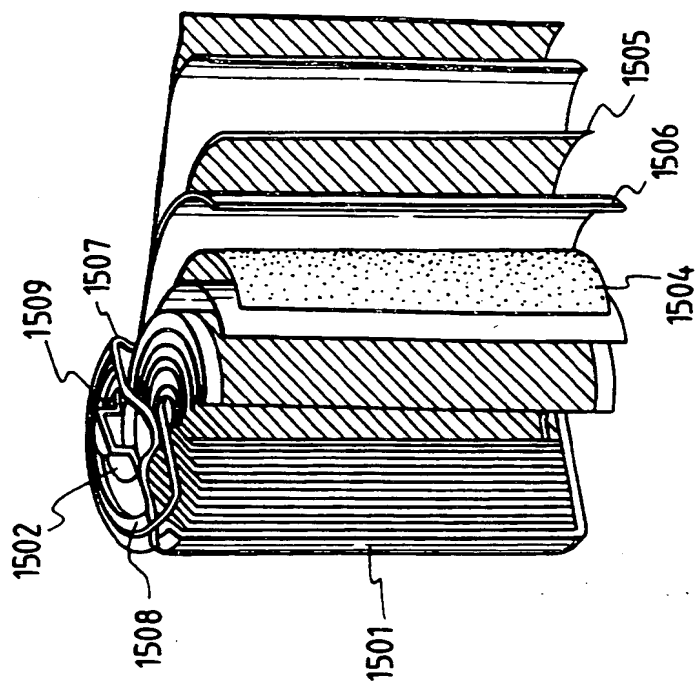


FIG. 14

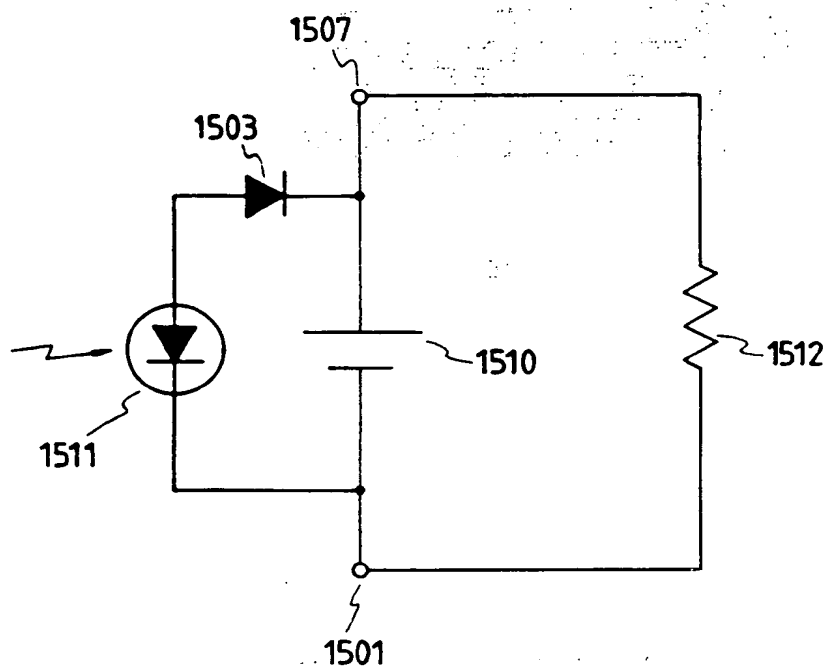


FIG. 15

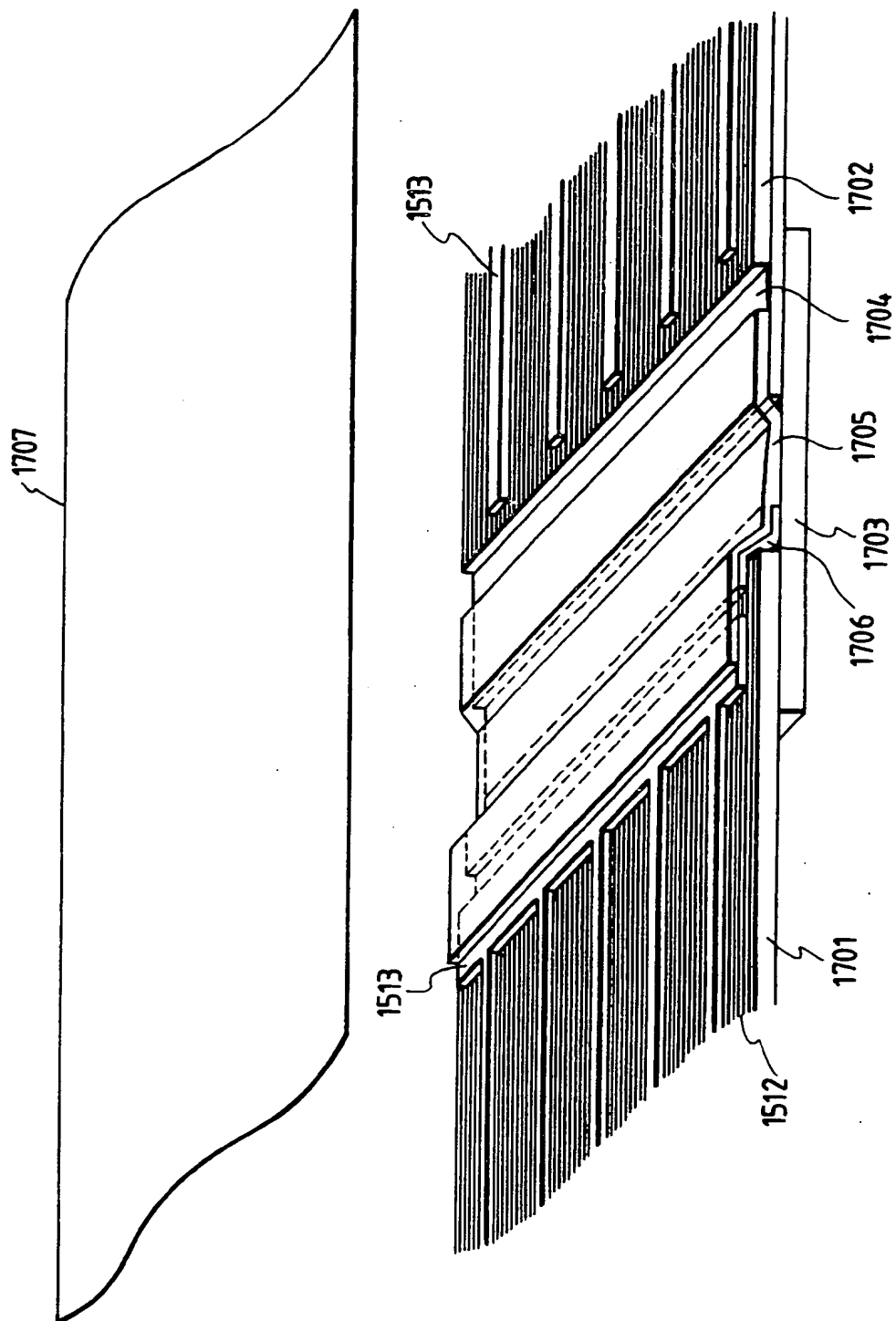


FIG. 16

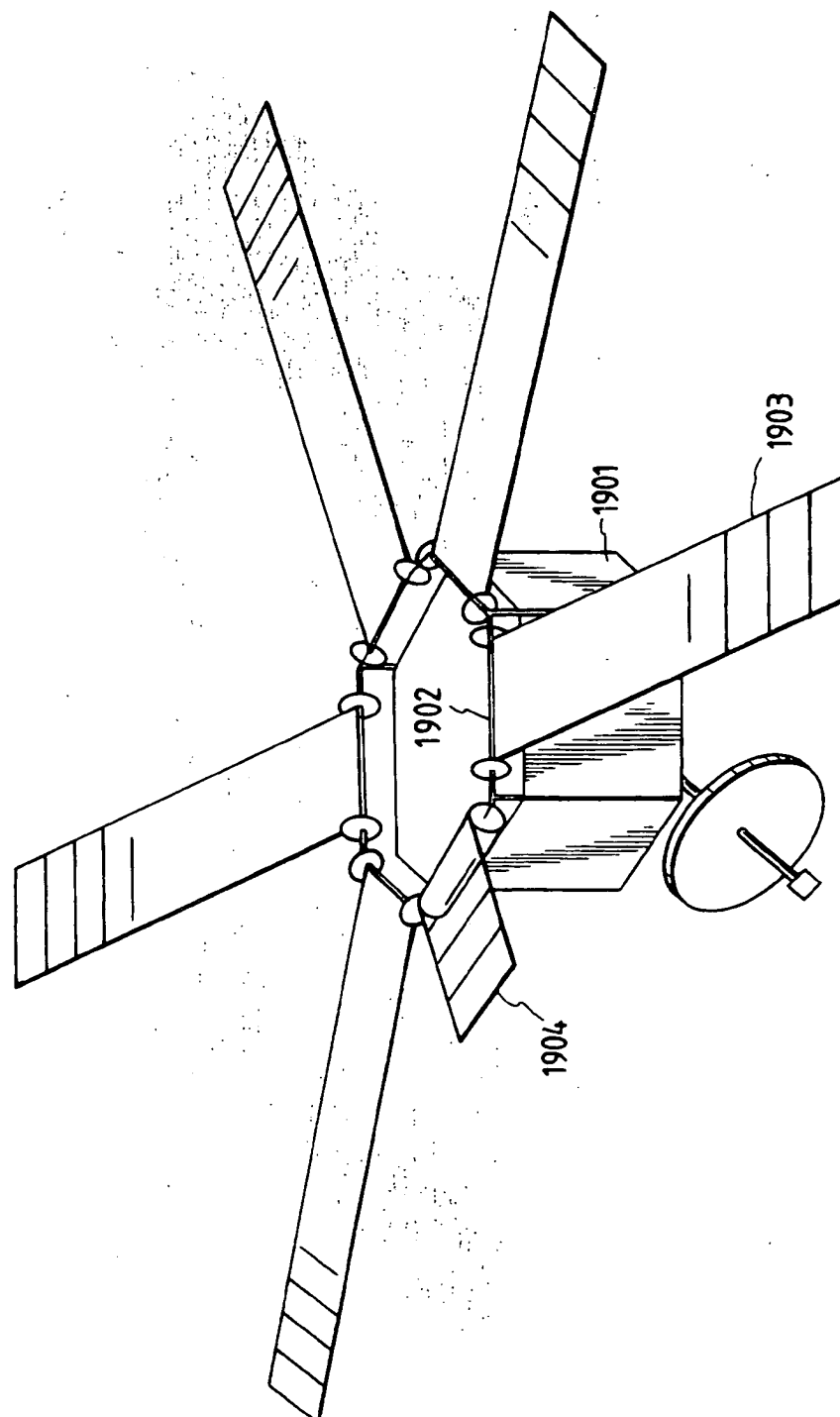


FIG. 17

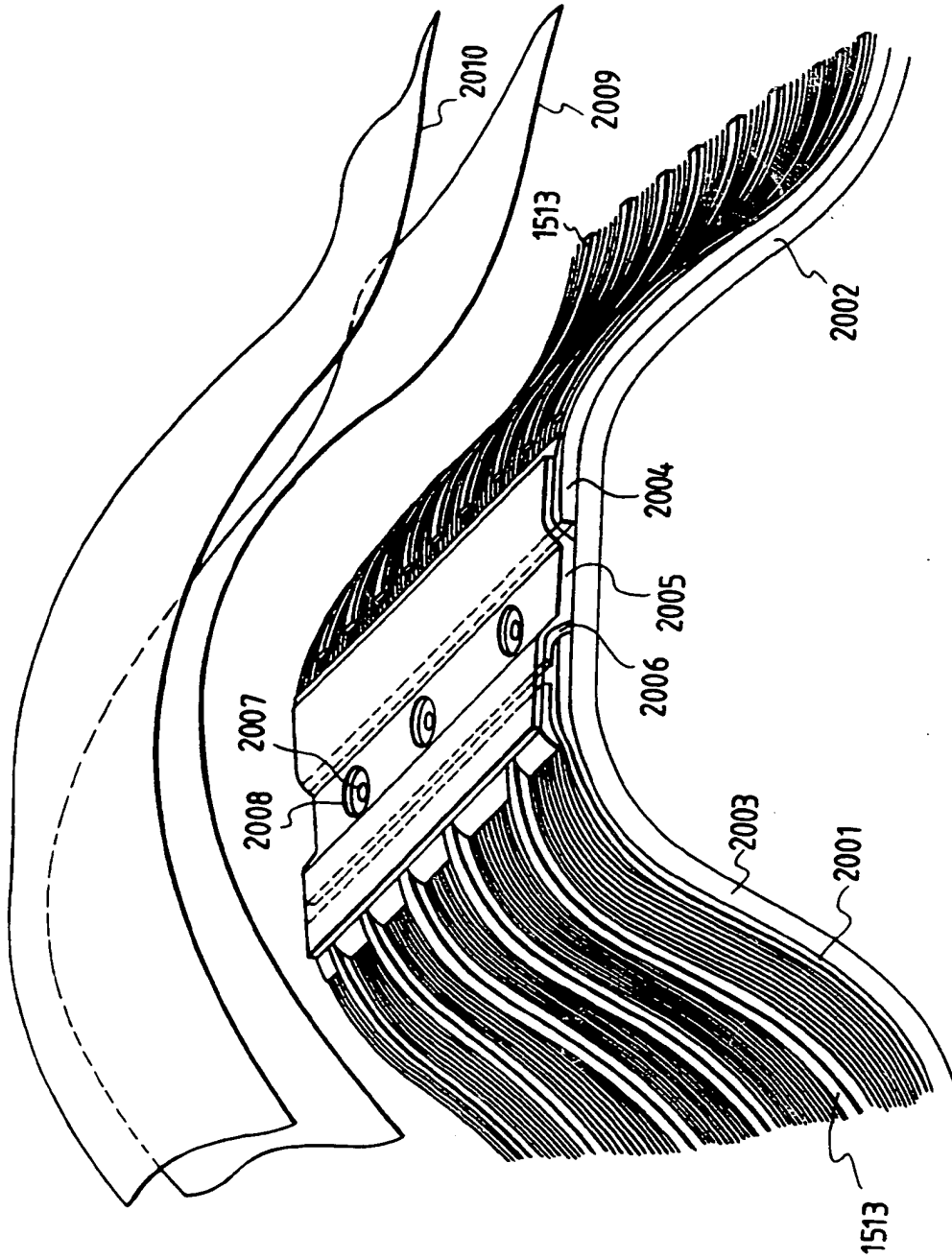


FIG. 18

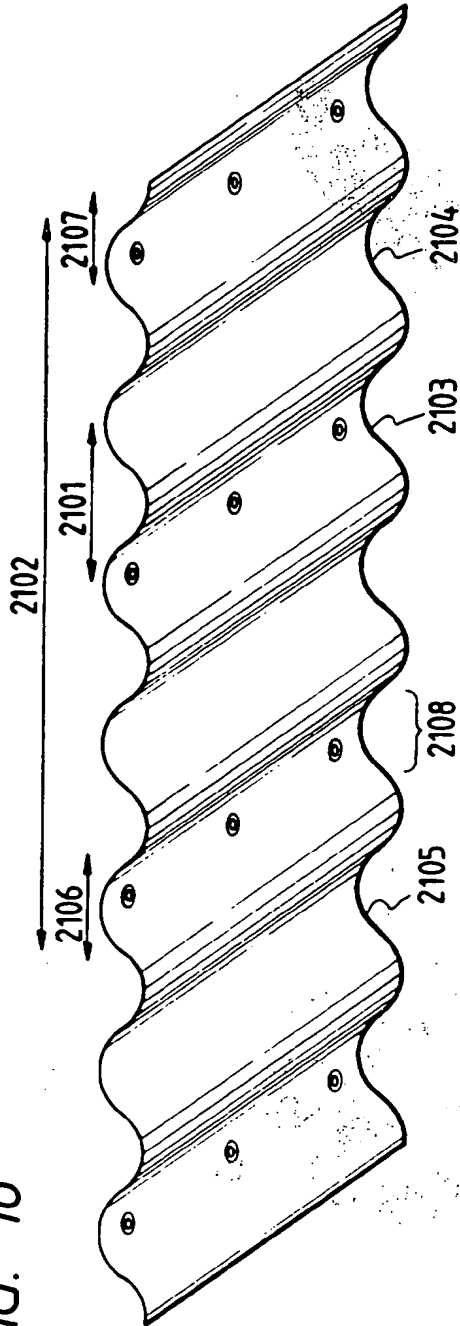


FIG. 19

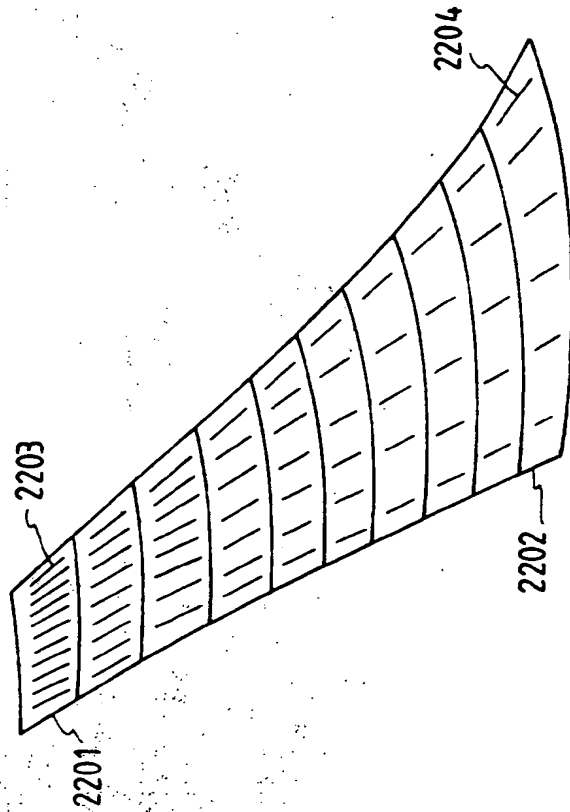


FIG. 20

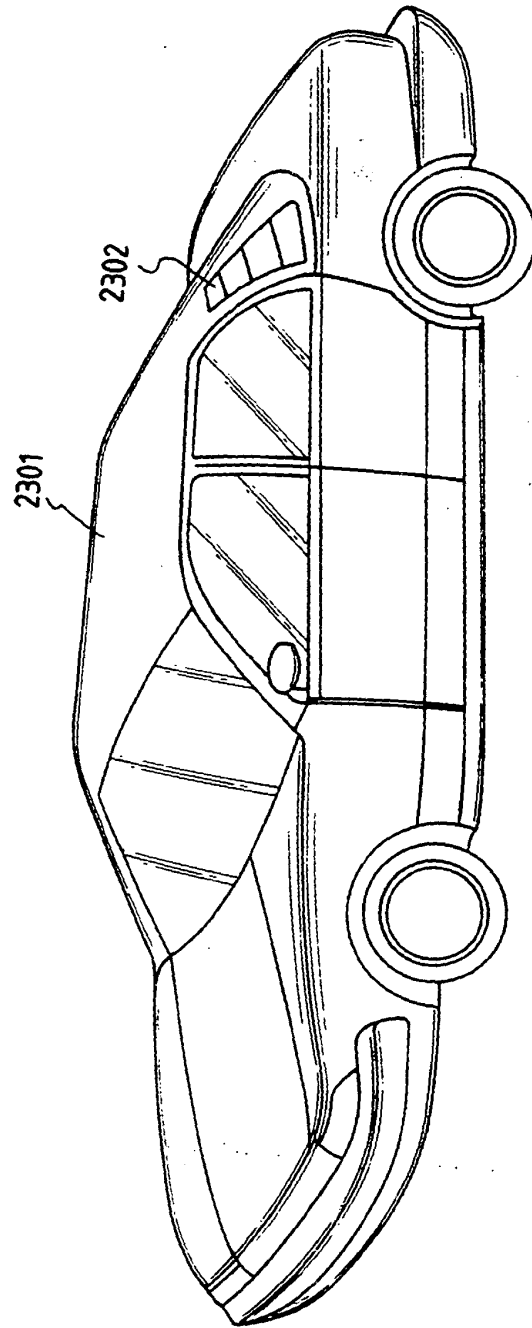
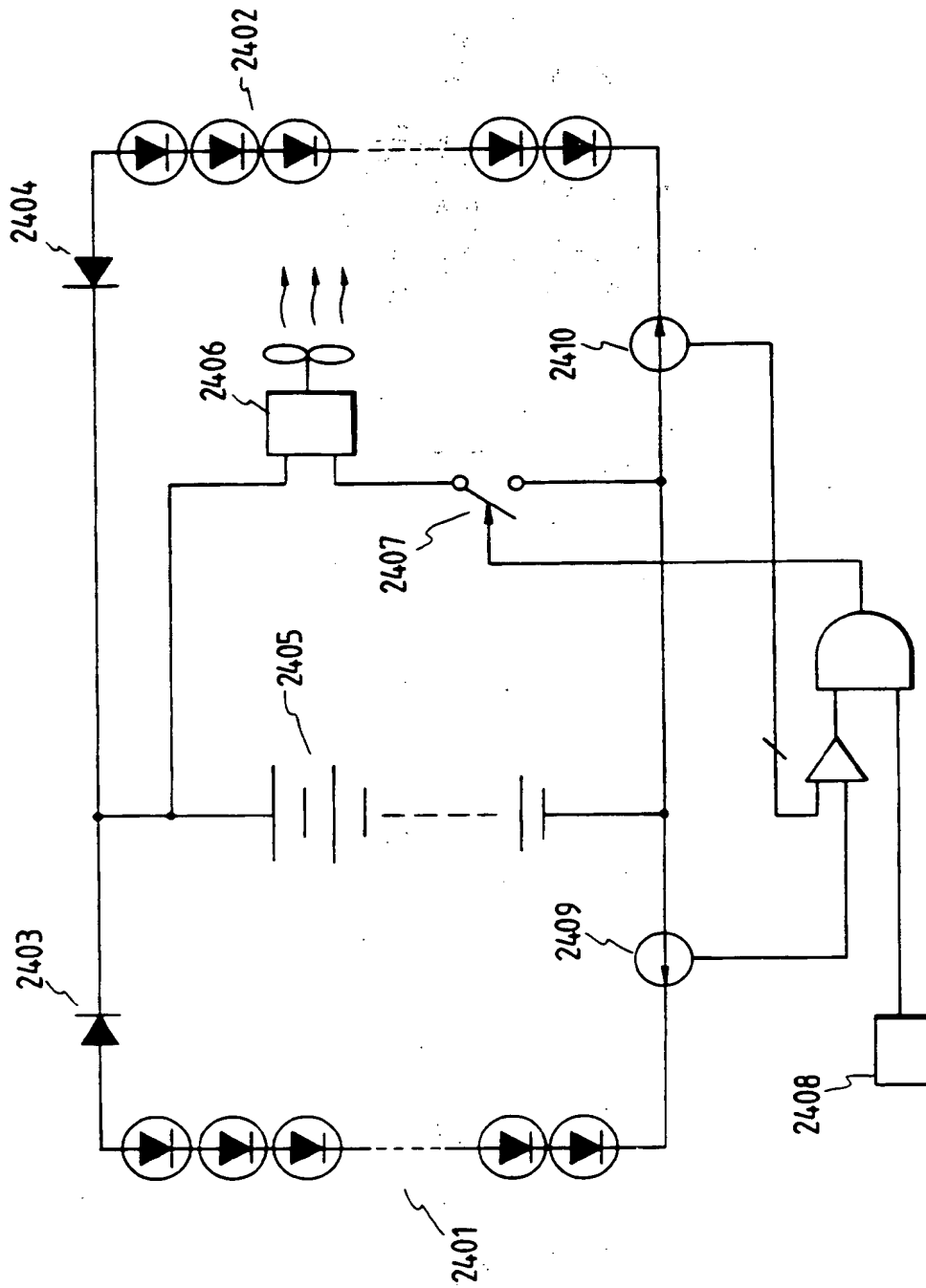


FIG. 21





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 93101759.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US - A - 5 064 477 (DELAHOY) * Claims 1-10 *	1, 13, 14, 17- 23	H 01 L 31/18
P.A	US - A - 5 078 804 (CHEN et al.) * Claims 1-3, 12, 18 *	1, 13, 14, 17- 23	
P.A	US - A - 5 078 803 (PIER et al.) * Abstract *	1, 13, 14, 17- 23	
A	US - A - 4 612 411 (WIETING et al.) * Abstract *	1, 13, 14, 17- 23	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			H 01 L 31/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 22-04-1993	Examiner BRUS
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same family A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			